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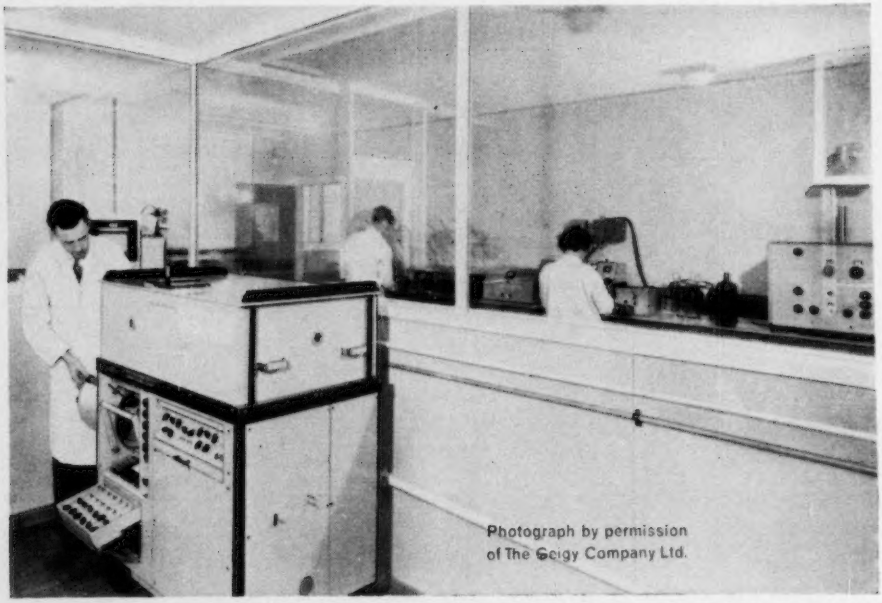

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ANALYTICAL ABSTRACTS

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3562. **Congress for analytical chemistry. Sections VIIb to VIII.** Held at Budapest, April 24–29, 1961. *Acta Chim. Acad. Sci. Hung.*, 1961, **28** (1–3). The following papers are included (in German unless otherwise stated).

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3563. **The correct determination of errors and confidence intervals of indirect analyses.** P. Görlich (Hauptlab. der Österreich. Stickstoffwerke A.-G., Linz). *Z. anal. Chem.*, 1961, **179** (4), 266–276 (in German).—Indirect analyses depend upon the solution of systems of linear equations of the type $a_{m1}.\bar{x}_1 + a_{m2}.\bar{x}_2 \ldots\ldots\ldots\ldots + a_{mk}\bar{x}_k = \bar{y}_m$. The best method of assessing the accuracy of such determinations is by calculation of the confidence interval of the mean μ_y from the t distribution. For the determination of t the number of degrees of freedom f is required, and it is shown that the usual method of determining f is not valid because the values of s_g originate from entirely different populations. Therefore f should be obtained from the expression given by Welch (*Biometrika*, 1949, **36**, 293). The method of calculation is described, and illustrated by results for a gypsum mineral.

A. J. Bennett

3564. **Pyrrolidine derivatives as organic reagents in inorganic analysis. III. Typical reactions of rhodanines.** B. M. Turkevich. *Farm. Zhur.*, 1960, (1), 15–20; *Ref. Zhur., Khim.*, 1960, (20), Abstr. No.

80,705.—The reactions of various cations with 50 rhodanines and 10 thiazolidine-2,4-diones were studied. Test soln. (0·01-ml aliquots ≡ ≮ 10 μg of cation) were placed on filter-paper impregnated with 0·001M soln. of the reagents, and the resulting spots were inspected in visible and u.v. light. The rhodanines are group reagents for Ag^+, Hg_2^{2+}, Hg^{2+}, Cu^+, Cu^{2+}, Au^{3+}, Pd^{2+} and Pt^{4+}, the analytically functional groups being –CO·NH·CS– and $-CH_2{\cdot}S{\cdot}C(:S){\cdot}N<$. Substitution in the 3-position may increase or decrease the sensitivity of the reaction, but does not deprive the reagents of their reactivity, indicating complex formation. The analytically functional group for Os^{VIII} is the grouping $-CH_2{\cdot}S{\cdot}C(:S){\cdot}NH-$, substitution of the hydrogen atom by organic radicals causing loss of activity. The salicylidene and β-hydroxy-α-naphthylidene groups are analytically active for Os^{VIII}; in the u.v. region the spots have a blue colour with marked fluorescence. The thiazolidine-2,4-diones are group reagents for Au^{3+}, Pd^{2+}, Cu^{2+}, Ag^+, Hg_2^{2+}, Hg^{2+}, Pt^{4+}, La^{3+} and UO_2^{2+}. The most sensitive reagent for Ag^+ is 3-allyl-5-*p*-dimethylaminobenzylidenerhodanine; the detectable minimum is 0·0001 μg of Ag. (For Part II see *Ref. Zhur., Khim.*, 1960, Abstr. No. 56,647.)

C. D. KOPKIN

3565. **Bathophenanthrolinedisulphonic acid and bathocuproinedisulphonic acid, water-soluble reagents for iron and copper.** D. Blair and H. Diehl (Dept. of Chem., Iowa State Univ., Ames, U.S.A.). *Talanta*, 1961, **7** (3–4), 163–174 (in English).—Bathophenanthroline- and bathocuproine-disulphonic acids (**I** and **II**) have been isolated and characterised as their sodium salts. The method for the determination of Fe^{2+} with **I** described by Trinder (*Anal. Abstr.*, 1956, **3**, 3135) was satisfactory for $HClO_4$ soln. from the wet-ashing of biological material. Interference by 16 cations and 18 anions was studied; most common ions have little effect. Similar studies were carried out on the determination of Cu^{2+} with **II**.

P. D. PARR-RICHARD

3566. **Concentrating traces of copper from M-ammonium chloride.** R. Turse and W. Rieman, III. (Rutgers State Univ., New Brunswick, N.J., U.S.A.). *Anal. Chim. Acta*, 1961, **24** (2), 202–203 (in English).—Bivalent Cu is removed from M-NH_4Cl by passing the soln. (1 ml) through a column (area 0·94 sq. cm) of Dowex chelating resin A-1, and is recovered by elution with M-HCl (10 ml). When the vol. of resin is >1·0 ml and the flow rate of the soln. <3·8 cm per min., the recovery is ≮99·0%.

H. N. S.

3567. **Qualitative inorganic analysis. XVIII. The removal of thiosulphate ion.** W. F. Jones (Sci. Dept., Victoria Inst., Worcester, England). *Mikrochim. Acta*, 1961, (2), 214–216 (in English).—The sample is boiled with 4N-HCl. This decomposes complex thiosulphates and produces a ppt. containing S, from which $PbCl_2$ is extracted with boiling water, CuS, Cu_2S and As_2S_3 with boiling 4N-HNO_3, AgCl with aq. NH_3, and Hg_2Cl_2 with boiling aqua regia. The residue may be further examined for $BaSO_4$ and other insoluble substances. The filtrate is diluted to precipitate AgCl and $PbCl_2$, which are appreciably soluble in 4N-HCl.

W. T. CARTER

3568. **Analysis for industry.** T. S. West. *Ind. Chem.*, 1960, **36**, 559–561; 613–615.—Developments and applications in the use of metallochromic indicators for Ca and Mg, and of metallofluorescent indicators, dyestuffs and intermediates used in EDTA titrations, are reviewed. (57 references.)

S.C.I. ABSTR.

3569. **Purification of dimethylformamide for use in non-aqueous titrations.** R. E. Moskalyk, L. G. Chatten and M. Pernarowski (Food & Drug Lab., Dept. of Nat. Health & Welfare, Ottawa, Ontario, Canada). *J. Pharm. Sci.*, 1961, **50** (2), 179.—To remove acidic impurities from dimethylformamide, stir 500 ml with Dowex 1-X10 (OH^- form) (50 g) in a stoppered flask for several hours, decant and filter. By this treatment, the blank titre for a 50-ml sample is reduced from 0·4 ml to 0·05 ml of 0·1N-methanolic KOH.

A. R. ROGERS

3570. **Ionisation methods for the analysis of gases and vapours.** J. E. Lovelock (Nat. Inst. for Med. Res., Mill Hill, London). *Anal. Chem.*, 1961, **33** (2), 162–178.—The physical basis, design and construction, performance and applications of different types of ionisation detector are thoroughly examined. (39 references.)

C. B. BAINES

3571. **Notes on the use of the silver reductor.** I. Korondán and J. Zýka (Inst. Anal. and Inorg. Chem., Univ. Debrecén, Hungary). *Z. anal. Chem.*, 1961, **179** (3), 161–164 (in German).—Quantitative reduction of Ti^{4+} by the silver reductor occurs at 80° to 90° in soln. > 7N in HCl and 3·2N in acetic acid. Acetic acid forms a complex with Ti^{3+} which is less readily oxidised by air. The method is applied to the determination of Ti in ferrotitanium. *Procedure*—Dissolve the sample (1·0 g) in 10% H_2SO_4 (50 ml) and oxidise with conc. HNO_3. Filter off insoluble carbon, evaporate the filtrate to fumes, dissolve the residue in water and evaporate again. Dissolve the residue in water and dilute to 100 ml. To 5 ml of the soln. add 11 ml. of conc. HCl and 4 ml of glacial acetic acid and pass the mixture through the silver reductor at a temp. of 85° and a rate of 2 ml per min. Wash the reductor 4 times with 8N-HCl. Titrate the combined soln. and washings potentiometrically with 0·1N-$(NH_4)_2SO_4.Fe_2(SO_4)_3$ in a stream of CO_2. The average error is 0·75%; Mo^{6+}, U^{6+}, W^{6+} and F^- interfere.

A. J. BENNETT

See also Abstract—**3745**, Respropiophenone oxime as a reagent for Ni. **3769**, Use of alizarin complexan. **3800**, Organophosphorus extractants.

2.—INORGANIC ANALYSIS

General, determination of elements (arranged in the order of the Periodic Table), analysis of minerals and inorganic industrial products.

3572. **Gas-chromatographic analysis of permanent gases using standard ionisation detector equipment.** R. A. Landowne and S. R. Lipsky (Dept. of Internal Med., Yale Univ. School of Med., New Haven, Conn., U.S.A.). *Nature*, 1961, **189**, 571–572.—A standard 1 cm × 1 cm ionisation detector (*cf.* Lovelock, *Anal. Abstr.*, 1958, **5**, 3208) with a 100-mC ^3H source is used with ordinary commercial He instead of Ar as carrier gas. An applied potential of ≃500 V, which gives a standing current of 10^{-8} amp. and a noise level of 5×10^{-11} amp. at room temp., may be used. Introduction of O, N, H, NO, CO, CO_2, methane or ethylene into the carrier stream causes a decrease in the standing current, probably by quenching the secondary electrons.

The detector is sensitive to $\simeq 10^{-9}$ mole of permanent gas per sec., and the response is linear up to $\simeq 10^{-6}$ mole per sec. By use of a calibration curve, quant. results can be extended beyond the linear range by at least a factor of five. A. R. ROGERS

3573. **Vacuum fusion analysis with a platinum bath for the determination of gases in metals.** Z. M. Turovtseva, N. F. Litvinova, N. M. Vasil'eva and K. G. Semenyuk. *Trudy Komiss. Anal. Khim., Akad. Nauk SSSR*, 1960, **10**, 109–116; *Ref. Zhur., Khim.*, 1960, (24), Abstr. No. 96,162.—The advantages of a platinum bath are shown, and conditions are described for the determination of gases in certain metals. For beryllium, a 2 to 10-mg sample is used, at 1900°, with an extraction time of 5 to 7 min.; the allowable ratio of Pt to Be is 50:1. The samples are dropped into the crucible, which must be closed tightly, at a lower temp. For silicon, a 100 to 300-mg sample is used, at 1800°, with an extraction time of 10 min.; for tantalum, a 30 to 200-mg sample, at 2000°, for 10 min.; for uranium, a 5 to 20-mg sample, at 1900°, for 10 min. (the concn. of U must not exceed 30%); for yttrium, a 5 to 50-mg sample, at 1800°, for 10 min. C. D. KOPKIN

3574. **Evaluation of the extent of extraction in the determination of gases in metals by means of vacuum fusion.** Yu. A. Klyachko and E. M. Chistyakova (I. P. Bardin Central Sci. Res. Inst. of Ferrous Metall.) *Zavod. Lab.*, 1961, **27** (2), 135–138.—Gases liberated from two different kinds of steel (U 12 and St. 3) and metallic manganese were studied, (*a*) with the use of tin, nickel and iron-molybdenum baths at 1650° for U 12, the tin bath giving the best results for H and the nickel bath the best results for O and N; (*b*) with the use of nickel and tin baths for St. 3, both giving satisfactory results; and (*c*) with the use of iron (1550°) and copper (1100°) baths for manganese, the latter being preferred. G. S. SMITH

3575. **Determination of hydrogen, oxygen and nitrogen in metals by fusion under reducing conditions in an argon atmosphere.** J. Hancart and J. Marot (Section du Hainaut, Centre Nat. de Rech. Métallurgiques). *Rev. Métall.*, 1960, **57** (10), 911–917.—*Determination of O and N*—A furnace containing a graphite crucible is purged by a slow upward current of Ar. The sample is dropped into the crucible, the flow of Ar is stopped and the temp. maintained at 1750° for 20 min. The gases are then swept into a gas holder by a stream of Ar (2 litres per min.) and the amounts of N and CO present in 35-ml aliquots of the gas mixture are determined by gas chromatography. The results of the O determinations agree with those obtained by vacuum fusion, and the reproducibility of the N determinations is 6×10^{-4} %. *Determination of H*—The sample is de-gassed in Ar in a small tubular furnace at 650°. The amounts of H produced during successive 10-min. periods are determined by gas chromatography until a constant blank value is reached. A. J. BENNETT

3576. **Inorganic thin-film chromatography. I.** H. Seiler and M. Seiler (Anst. für Anorg. Chem., Basel Univ., Switzerland). *Helv. Chim. Acta*, 1960, **43** (7), 1939–1941 (in German).—The application of this method to the separation and identification of cations that give ppt. in (*a*) acid and (*b*) alkaline sulphide soln. is described. Silica gel (500 g) is purified by being washed with 1 litre of 50% HCl, then with water and finally with light petroleum. After being dried at 120°, the gel (28 g) is mixed with 2 g of plaster of Paris and made up into a paste with 15 ml of water, which is then applied as a strip on a glass plate and dried over $CaCl_2$ overnight. A convenient volume of test soln. for application is 0·004 ml of 0·1M concn. For separation of the H_2S-group cations, the developing agent is butanol - 1·5N-HCl - acetonylacetone (200:40:1). The developed chromatogram is sprayed with 2% KI soln., and then treated first with NH_3 gas and then with H_2S to produce colours characteristic of the H_2S-group cations. For the $(NH_4)_2S$-group cations, the developing agent is acetone - conc. HCl - acetonylacetone (200:2:1). The chromatogram is treated with NH_3 gas, then sprayed with a 0·5% soln. of 8-hydroxyquinoline in 60% ethanol and observed in daylight and under u.v. light. J. L. PROSSER

3577. **Experimental contribution to the catalytic determination of trace metals.** J. Laszlovszky (Inst. Inorg. and Anal. Chem., L. Eötvös Univ., Budapest, Hungary). *Mikrochim. Acta*, 1961, (2), 289–295 (in German).—A study of the reaction between alizarin and sodium perborate or H_2O_2 at pH 10·4 (*Anal. Abstr.*, 1960, **7**, 3767) has shown that, in the absence of catalytic amounts of Co, the rate of thermal decomposition of the peroxide at 90° is decreased by the addition of alizarin. The reaction can be followed by the change in colour of the soln. or by the change in concn. of peroxide. W. T. CARTER

3578. **Flame-photometric determination of small amounts of metal diethyldithiocarbamates after extraction with carbon tetrachloride.** E. Schöffmann and H. Malissa (Chem.-metall. Versuchsanst., Niederrhein. Hütte A.-G., Duisburg, Germany). *Mikrochim. Acta*, 1961, (2), 319–322 (in German).—Iron, Cu, Co, Ni and V are determined by extraction with CCl_4 from 0·1N-HCl soln. containing Na diethyldithiocarbamate. The CCl_4 extract is analysed in a Beckman spectrophotometer with flame-photometer attachment. The metals are determined by measuring the emission at the following wavelengths—Fe 372·0 mμ, Cu 324·8 mμ, Co 353·0 mμ, Ni 352·5 mμ and V 576·0 mμ. The relationship between metal concn. and emission intensity is linear up to 200 μg, and the reproducibility at the 100-μg level is ± 0·4 to 0·7 μg. W. T. CARTER

3579. **Successive radiometric titration of several elements with the sodium salt of 3-methyl-5-phenylpyrazoline-1-carbodithioic acid containing sulphur-35.** A. I. Busev and V. M. Byr'ko. *Izv. Vyssh. Ucheb. Zavedenii, Khim. i Khim. Tekhnol.*, 1960, **3** (1), 52–55; *Ref. Zhur., Khim.*, 1960, (20), Abstr. No. 80,722.—This reagent is used for the successive radiometric titration by the precipitation method of combinations of a number of elements (Tl^{3+} - In^{3+}; Tl^{3+} - Zn^{2+}; Cd^{2+} - Zn^{2+}), of which one (Tl or Cd) is completely pptd. at pH ≃ 14 from tartrate soln., and the other (In or Zn) only at lower pH values (≃7). By using the isotopes ^{204}Tl and ^{65}Zn, new forms of radiometric titration curves have been obtained. C. D. KOPKIN

3580. **Spectrophotometric determination of copper, nickel, cobalt, iron and manganese as their pyridine thiocyanates. Simultaneous determination in mixtures.** G. H. Ayres and S. S. Baird (Dept. of Chem., Univ. Texas, Austin, U.S.A.). *Talanta*, 1961,

7 (3–4), 237–247 (in English).—The pyridine thiocyanates of Cu, Ni, Co, Fe^{2+} and Mn^{2+} give absorption bands at 405, 360, 335, 375 and 300 mμ, respectively; the extinctions are additive when sufficient pyridine and SCN^- is present. *General procedure*—To 100 ml of soln. (< 1 mg of Cu, Co or Fe, ≃2 mg of Mn, or ≃40 mg of Ni) add 10% tartaric acid soln. (25 ml), 50% $Mg(NO_3)_2$ soln. (6 ml), pyridine (8 ml), 10% KSCN soln. (8 ml) and NaOH to give a pH of 5 to 7. Extract with $CHCl_3$ (3 × 10 ml), dilute the combined extracts to 40 ml, and clarify with a little acetone. Dilute to 50 ml with $CHCl_3$ and measure the extinction. Phosphate, Br^-, I^-, OCN^- and CN^- should be absent. P. D. PARR-RICHARD

3581. **Chemical - spectrographic determination of bismuth, cadmium, antimony, tin and lead in tungsten, niobium and tantalum.** D. I. Ryabchikov, É. E. Vainshtein, L. V. Borisova, M. P. Volȳnets, V. V. Korolev and Yu. I. Kutsenko. *Trudȳ Komiss. Anal. Khim., Akad. Nauk SSSR*, 1960, **12**, 82–93; *Ref Zhur., Khim.*, 1961, (3), Abstr. No. 3D156.—*Procedure with tungsten*—Oxidise the metal powder (1 g) by heating for 30 to 40 min. at 600°. Dissolve the oxide by heating in 30% NaOH soln. (4 ml), add 30% tartaric acid soln., adjust to pH 2 and add $Cu(NO_3)_2$ soln. (0·15 ml) (100 mg of Cu per ml) as a carrier. Pass H_2S through the soln., allow the ppt. to settle for 30 min., then filter and wash the ppt. with H_2O (40 ml) acidified with HCl and satd. with H_2S. Add Cu (15 mg) to the filtrate, pass H_2S through, filter, wash and dry the filter plus ppt., and finally ignite for 40 min. at 500°. Weigh the residue. *With niobium or tantalum*—Oxidise the metal powder (1 g) for 40 min. by ignition in a quartz crucible at 600°; fuse the oxide with $K_2S_2O_7$ (25 g for niobium, 60 g for tantalum) for 15 min. at 600° till a transparent melt is obtained. Leach the niobium melt by heating with tartaric acid soln. (10%) (60 ml) (25% citric acid for a tantalum melt), add the carrier described above and pass H_2S. Wash the residue on the filter with H_2O (60 ml) satd. with H_2S and continue as described above. An alternative method is to treat niobium and tantalum with HF in a platinum dish. Place 20 mg of the residue in the crater (diam. 3·5 mm, depth 5 mm) of a carbon anode, excite spectra at 6 amp. for 60 sec. and photograph the spectra in a medium spectrograph with a slit width of 5 μ. Construct calibration curves with standards similarly treated with the lines Cd 3261·1, Sb 2598·1, Sn 3175·0, Pb 2614·2 (for W) and 2833·1 (for Nb and Ta) and Bi 3067·6. The background serves as the comparison element; the sensitivity of a determination with a 20-fold enrichment is 10^{-4} %, except with Sb, when it is less. The error is ± 20%. K. R. COOK

3582. **Ion-exchange extraction with high-molecular-weight amines. I. Extraction of iron(III), nickel, cobalt and zinc from hydrochloric acid solution.** Genkichi Nakagawa (Nagoya Inst. of Tech., Gokiso-cho, Showa-ku). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1960, **81** (3), 444–446.—The extraction of Fe^{III} with dodecenyltrialkylammonium chloride (**I**) in kerosine (10%) is facilitated by an increase in concn. of HCl and becomes quant. between 6 and 10N. The optimum HCl concn. for the extraction of Zn is 2 to 3N (≃90%), and the percentage decreases with increase in HCl concn. Bivalent Co is extracted from soln. >5N in HCl and ≃35% is extracted from soln. 8N in HCl; Ni is not extracted. Both Fe and Zn are back-extracted with 0·5N-HNO_3. The apparent relationship between these results and those of Kraus is discussed.

II. Extraction of tellurium from hydrochloric acid solution. Genkichi Nakagawa. *Ibid.*, 1960, **81** (3), 446–448.—Although Te^{IV} is quant. extracted with **I** (10%, w/v) in xylene from soln. >6N in HCl, Te^{VI} is not extracted from soln. <10N in HCl. In a more conc. HCl soln., Te^{VI} is reduced to Te^{IV} and is partly extracted with **I**. The Te^{IV} is back-extracted with water or dil. HNO_3.

III. Extraction of aluminium, titanium(IV) and iron. Genkichi Nakagawa. *Ibid.*, 1960, **81** (5), 747–750.—Aluminium is not extracted with **I** in kerosine from either HCl or H_2SO_4 soln. Only part (≃10% at 11·8N) of Ti^{IV} is extracted from soln. >8N in HCl and none from H_2SO_4 soln. Less than 20% of Fe^{II} is extracted from soln. >N in HCl, to an extent that increases with increase in HCl concn. Tervalent Fe is best extracted (≃90%) from soln. 0·025 to 0·05M in H_2SO_4; the amount decreases with decrease or increase in the concn. of acid, reaching zero with 0·05M-H_2SO_4. The separation of Fe^{III} from Al and Ti is effected by extraction from soln. 6N in HCl.

IV. Extraction of arsenic, antimony and bismuth from hydrochloric acid solution. Genkichi Nakagawa. *Ibid.*, 1960, **81** (5), 750–753.—Although As^V is not extracted with **I** in kerosine (10%, v/v), some As^{III} is extracted from soln. >4N in HCl, and ≃92% from soln. 8 to 11N in HCl. Tervalent Sb is almost quant. extracted from soln. 1 to 4N in HCl, but to a less extent from a more conc. acid; the extraction of Sb^V is facilitated by an increase in HCl concn. and is quant. from soln. >6N in HCl. Bismuth is completely extracted from soln. 0·3N in HCl, and the percentage decreases with increase in HCl concn., reaching ≃ 0% at acid concn. of 10N. Tervalent As is back-extracted with water and dil. HNO_3. Sb^{III} and Bi with 0·5M-citric acid, and Sb^V with M-NaOH, but not with mineral acids. K. SAITO

3583. **Extraction of cobalt, zinc and cadmium xanthates.** F. R. Sheyanova, A. G. Airapetyan, S. A. Ryabova and V. M. Ryabov. *Trudȳ Khim. i Khim. Tekhnol.*, 1959, (2), 410–413; *Ref. Zhur., Khim.*, 1960, (23), Abstr. No. 91,995.—The radioactive isotopes ^{60}Co, ^{65}Zn and ^{115}Cd are used in studying the influence of pH on the completeness of extraction of the ethyl-, isopropyl-, butyl-, isoamyl- and benzyl-xanthates of Co, Zn and Cd with $CHCl_3$, with a vol. ratio of H_2O to $CHCl_3$ phases of 3:1 and with a 100 to 500-fold excess of reagent. With K ethylxanthate at pH 1 only Co is extracted, and at pH >10 Cd can be separated from large amounts of Zn. Owing to the large excess of reagent used, other xanthates did not give results significantly different from those given by ethylxanthate for the extraction of Co, Zn and Cd. Extraction is practically complete with benzylxanthate, at pH 0·85 to 5·2 for Co, and 1·9 to 5·2 for Zn and Cd. C. D. KOPKIN

3584. **Simultaneous estimation of several radioactive nuclides.** C. W. Gilbert. *Int. J. Appl. Radiation and Isotopes*, 1960, **8** (4), 130–132.—A method is described in which simultaneous equations relating unknown activities are solved to give a simple expression for each nuclide, the concn. of which can then be derived by substituting the readings, recorded with suitable detectors, in the

expression. Results are quoted for the analysis of mixtures of ^{32}P and ^{59}Fe. G. J. HUNTER

3585. **Assay of granular materials for water content by means of neutron retardation.** A. K. Val'ter and M. L. Gol'bin. *Atomnaya Energiya*, 1960, **8** (3), 248–249.—The method is sensitive and rapid. The measurements are independent of the presence of other elements with $Z > 5$ (except for strong absorbers of neutrons) and of the density or mass of the absorbent. The stream of slow neutrons is registered on a scintillation counter; the neutron retardation rate is a function of the water content of the test material. The source of fast neutrons is polonium - beryllium containing 1 curie of ^{210}Po ($2{\cdot}5 \times 10^6$ neutrons per sec.). A table is given showing the results of experiments with sand. The error rarely exceeds 0·5%. The results obtained were subjected to the interpolation formula: $I = 1225 + 4W + 1219W^2 - 1{\cdot}53W^3 + 0{\cdot}01W^4$, where W = moisture (wt. %) and I = impulses per min. K. R. COOK

3586. **Flame-spectrometric determination of potassium and sodium in clays.** F. Hegemann, H. M. Köster and G. Neubauer (Staatl. Forschungsinst. f. angew. Mineral., Regensburg, Germany). *Ber. dtsch. keram. Ges.*, 1960, **37**, 483–488.—Full details are given of the use of the Zeiss instruments PMQII and PF5. Suitable amounts of Al, Fe, Ca and Mg were included in the calibrating solutions so as to compensate for the interference by these elements. The sample solution was made with HF and H_2SO_4. J. A. SUGDEN

3587. **Determination of oxygen in alkali metals and their alloys by extraction with mercury.** E. D. Malikova and Z. M. Turovtseva. *Trudy Komiss. Anal. Khim., Akad. Nauk SSSR*, 1960, **10**, 91–96; *Ref. Zhur., Khim.*, 1960, (24), Abstr. No. 96,149.—The method is based on the use of amalgamation to remove alkali metal from its oxide. A sample of the molten metal is transferred by a medical syringe to a glass ampoule under a layer of nonane. Liquid Na - K alloy is sampled under vacuum. The ampoule with the sample (≃1·5 g) is placed in a column extractor, which is connected to a flask for the mercury by a ground glass joint; the apparatus is evacuated to a pressure of 10^{-4} torr, the ampoule is broken by magnetic means and mercury (≃40 ml) is run into the extractor. The extraction is repeated 8 or 10 times until the mercury no longer gives an alkaline reaction with phenolphthalein. The metal oxide is dissolved in water, and the soln. is titrated with H_2SO_4 to phenolphthalein. The apparatus is illustrated. The analysis requires 200 to 250 ml of mercury and takes 1 hr. The error is ≃ 10%. C. D. KOPKIN

3588. **Determination of oxygen in sodium and sodium - potassium alloy.** N. F. Litvinova, V. I. Malyshev and Z. M. Turovtseva. *Trudy Komiss. Anal. Khim., Akad. Nauk SSSR*, 1960, **10**, 97–102; *Ref. Zhur., Khim.*, 1960, (24), Abstr. No. 96,150.—The possibility of using the vacuum fusion method for the determination of O in alkali metals is shown. A method is developed for the determination of O in sodium and sodium - potassium alloy, of sensitivity 10^{-3} % by wt. and an accuracy of 15 to 20 %. C. D. KOPKIN

3589. **The use of *p*-anisidine for the quantitative determination of copper.** V. N. Podchalnova. *Trudy Ural'sk. Politekh. Inst.*, 1959, (81), 192–211; *Ref. Zhur., Khim.*, 1960, (23), Abstr. No. 92,023.—The reaction of Cu^{2+} with *p*-anisidine in the presence of I^-, Br^-, Cl^- and SCN^- is studied for use in the photometric determination of Cu. Of the anions named, SCN^- is the most effective complexing agent as regards rate of formation and stability of the complex. C. D. KOPKIN

3590. **The use of *p*-anisidine in chemical analysis. II. Spot detection and determination of copper with *p*-anisidine.** V. N. Podchalnova. *Trudy Ural'sk. Politekh. Inst.*, 1960, (94), 134–140; *Ref. Zhur., Khim.*, 1960, (23), Abstr. No. 92,024.—The possible use of *p*-anisidine (**I**) for the detection, separation and determination of Cu^{2+} is studied. At pH 4·0 to 5·5, Cu forms a red - violet compound with a mixture of a satd. soln. of **I** and KSCN (1:1). The Cu content is determined visually or photometrically. No interference is caused by the presence of Fe^{3+}, Mn^{2+}, Zn, Al, Co or Ni. The average error in the determination of 0·02 to 0·5 mg of Cu is ≃ 0·01 mg. Milligram amounts of Cu (5 mg in 5 ml) can be separated from soln. containing Zn, Al, Cr, Mn, Co, Ni, Ca, Ba, Sr and Mg by **I** in the presence of SCN^- or by **I** alone. The resulting ppt. is dissolved by normal methods and Cu is determined iodimetrically; the mean error is ⩾ 2%. The mixture of **I** and KSCN can be used to detect Cu^{2+} in the presence of oxidising ions (CrO_4^{2-}, $Cr_2O_7^{2-}$, MnO_4^-, Fe^{3+}, Hg^{2+} and Au^{3+}). Cations are removed by pptn. with aq. NH_3 in the presence of NH_4Cl or glycine; Cu^{2+} are not co-pptd. Interfering anions are removed by reducing them to a lower valency. Nickel and Co in large amounts interfere so that, after removing interfering elements, the test soln. is diluted 5 or 6 times; the sensitivity of the reaction for Cu is then 5×10^{-6} g per litre. (*Cf.* Podchalnova and Loseva, *Anal. Abstr.*, 1960, **7**, 4126.) C. D. KOPKIN

3591. **Iodimetric determination of copper in hydrochloric acid medium.** V. N. Podchalnova and V. B. Avilov. *Trudy Ural'sk. Politekh. Inst.*, 1959, (81), 212–227; *Ref. Zhur., Khim.*, 1960, (24), Abstr. No. 96,118.—The influence of various factors on the behaviour of the systems Cu^{2+} - Cu^+ and $S_4O_6^{2-}$ - $2S_2O_3^{2-}$, which are of importance in the iodimetric determination of Cu_2 in HCl soln., is studied. The potential of the system Cu^{2+} - Cu^+ increases to 0·60 V with increase of the acidity of the soln. and of the concn. of I^- and SCN^- in the range 0·006 to 0·04M. The way in which the potential of this system changes is independent of the nature of the acid used. In the presence of KCl the greatest increase in the potential is in HCl medium. Copper contents of 0·0012 to 0·012M can be determined in HCl medium with an accuracy of ≃4%. To determine Cu in copper metal, dissolve 0·1 g of sample in 5 ml of HCl (sp. gr. 1·19) containing 5 drops of 30% H_2O_2 soln., dilute to 100 ml, boil for 5 min., cool, add 0·5 g of KI, and titrate with 0·1N-$Na_2S_2O_3$. The mean relative error is 0·03 to 0·08%. To determine Cu in zinc and aluminium alloys, to the soln., after dilution to 100 ml, add 0·03 g of KSCN, 0·2 to 0·3 g of NaF and 0·5 g of KI. Cover the beaker, set aside for 5 min., and titrate with 0·1N- or 0·01N-$Na_2S_2O_3$ to a straw-yellow colour; add 1 ml of 1% starch soln. and titrate with the $Na_2S_2O_3$ soln. to a pale-violet colour; add 0·5 g of KSCN and titrate till colourless. The difference between the results by the electrogravimetric and the described methods is ⩾ 0·04%. C. D. KOPKIN

3592. **Reaction of copper and bismuth ions with 2-mercaptobenzimidazole.** V. N. Podchalnova and O. N. Chupakhin. *Trudy Ural'sk. Politekh. Inst.*, 1959, (81), 184–191; *Ref. Zhur., Khim.*, 1960, (23), Abstr. No. 92,009.—Procedures are developed for the spot detection of Cu^{2+} and Bi^{3+} with 2-mercaptobenzimidazole (**I**), in the presence of other ions. With **I** in satd. Na acetate soln. (pH 6 to 7), Cu forms a blue ppt. or a bluish turbidity, depending on the copper content. A procedure is developed for the detection of Cu in zinc alloys by surface treatment, and milligram amounts of Cu can be completely separated from soln. containing large amounts of Ni and Co. Bismuth forms with **I** a bright-red water-insoluble complex. The reaction is independent of the pH of the medium, and takes place even in conc. HNO_3, thus allowing Bi to be detected in the presence of Cu. C. D. KOPKIN

3593. **Rapid spectrophotometric determination of copper in non-ferrous alloys.** G. Lindley (English Electric Co., Ltd., Bradford, Yorks., England). *Anal. Chim. Acta*, 1961, **24** (2), 161–166 (in English).—The Cu content of various non-ferrous alloys is determined by measuring the extinction at 950 mμ, due to $CuCl_4$, of a soln. of the alloy in conc. HCl (sp. gr. 1·18). Concn. of Cu down to 10 μg per ml in the final soln. can be measured. H. N. S.

3594. **Spectrophotometric determination of trace amounts of copper in tungsten metal powder.** A. S. Prokopovitsh and T. E. Green (Metallurgy Res. Center, College Park, Md., U.S.A.). *Rep. Invest. U.S. Bur. Min.*, 1961, No. 5720. 7 pp.—The sample (10 g) is dissolved in H_2O_2, tartaric acid (10 g) is added, the soln. is neutralised with 20% aq. NaOH and the pH is adjusted to 4 with H_2SO_4 (1:1). Excess of H_2O_2 is removed by boiling and 10 ml of each of the following reagents is added, with thorough mixing after each addition—5% aq. hydroxyammonium chloride, 30% aq. Na citrate and 0·1% ethanolic neocuproin (2,9-dimethyl-1,10-phenanthroline). The coloured copper complex is extracted into $CHCl_3$ and the extinction of the $CHCl_3$ soln. is read at 457 mμ against water. Copper contents as low as 1 p.p.m. can be determined, but the method is limited to finely divided tungsten powder. J. M. JACOBS

3595. **Interrupted a.c. arc for the quantitative spectrographic analysis of bronze.** E. A. Ratsbaum. *Trudy Leningrad. Lesotekh. Akad.*, 1960, (85), 85–91; *Ref. Zhur., Khim.*, 1960, (21), Abstr. No. 84,508.—The upper electrode, a copper wire of diam. 2·5 mm sharpened to a truncated cone, can be moved vertically; in its lowest extreme position it just touches the sample. The movement is brought about by a crankshaft driven by a single-phase motor, the drive being adjusted so as to extinguish the arc 7 times per sec., at a current strength of 3 amp. The image of the arc is projected on to the slit of spectrograph Q-24. From the spectra excited in the interrupted arc, rectilinear calibration curves are constructed from the lines Zn 3075 and Cu 3073, Pb 2833 and Cu 2882, and Sn 2913 and Cu 2882 A. The errors are, Zn, 5 to 10%, Pb, 10 to 15%, and Sn, 5 to 10%. Because of large variations in the values of ΔS, calibration curves cannot be constructed from spectra excited in the normal arc discharge. C. D. KOPKIN

3596. **Determination of traces of silver in high-purity lead.** B. L. Jangida, N. Mahadevan and C. Venkateswarlu (Anal. Div., Atomic Energy Estab., Trombay, Bombay). *J. Sci. Ind. Res., India, B*, 1961, **20** (2), 80.—Silver is extracted with dithizone, and the extinction is measured at 620 mμ; the mixed-colour method is employed. The addition of EDTA masks Pb and other metals. *Procedure*—Duplicate samples (5 g, or equiv. amounts of a Pb salt) are dissolved in 30 ml of HNO_3 (1:2). Solid EDTA (10 g) is added, and the pH is adjusted to 4·0 to 5·0 with aq. NH_3. To one soln., a suitable amount of Ag is added. Each soln. is transferred to a separating-funnel, and the pH is adjusted to 4·6 ± 0·1 by the addition of 5 ml of acetic acid - Na acetate buffer. The soln. are then extracted with 10 ml of dithizone (0·001% in CCl_4). The extinctions of the organic layers are measured at 620 mμ against a blank prepared from 5 ml each of aq. 2% EDTA soln. and buffer soln., diluted and extracted with 10 ml of dithizone soln. Copper, Zn, Cd, Bi, Fe and Ni do not interfere; 2×10^{-5} % of Ag can be determined. J. H. WATON

3597. **Determination of oxygen in silver surfaces.** G. Ströhl (Anorg. Chem. Inst., Tech. Hochschule, Braunschweig). *Z. anal. Chem.*, 1961, **179** (4), 259–262 (in German).—Silver wire (1 mm diam.) is washed in light petroleum, dried at 180° for 30 min., and then exposed to dry H_2S at 515° for 30 min. The O is converted into water according to the reaction $Ag_2O + H_2S \rightarrow Ag_2S + H_2O$; H_2S is removed from the reaction-chamber and absorption tubes by a stream of N and the water produced is determined micro-gravimetrically. Diffusion of H_2S into the metal is impossible, and diffusion of O from within the metal does not occur at 515°. Total O is determined by the hydrogen reduction method. In material having a specific surface of 3·84 sq. cm per g, the oxygen content of the surface was 0·0013 g per sq. metre. The surface oxygen of the material was ≃10% of the total oxygen and corresponded to a surface-layer thickness of $2·55 \times 10^{-6}$ mm of Ag_2O. A. J. BENNETT

3598. **Determination of gold in cyanide electrolytes.** M. A. Shashkin (Angara Mechanical Repair Works). *Zavod. Lab.*, 1961, **27** (2), 145–146.—A piece of zinc sheet is immersed in the soln. (5 to 100 ml) which is neutralised to litmus with 2N-H_2SO_4 and then treated with 1 g of pine charcoal and 4 to 6 ml of 2N-H_2SO_4, followed by 180 to 200 ml of water. The soln. is stirred for 50 min., the zinc is removed and the charcoal with adsorbed Au is filtered off, dried at 120° to 200° and ashed at 700° to 800° under oxidising conditions. The ash is mixed for 30 min. with 10 to 15 ml of a soln. of 2 g of iodine and 4 g of KI in 100 ml of water and the mixture is shaken with 3 to 4 g of mercury until the soln. is decolorised. Any ppt. of HgI_2 is dissolved by addition of 1 to 2 g of KI. The soln. is decanted and the mercury is washed and transferred to a porcelain crucible, where it is dissolved by addition of 2 to 3 ml of water and 6 to 8 ml of HCl-free HNO_3. The residual Au is washed with HNO_3 and water, and determined colorimetrically by the guaiacum resin method. G. S. SMITH

3599. **Determination of trace impurities in pure gold.** F. A. Pohl and W. Bonsels (AEG-Forschungsinst., Frankfurt, Germany). *Mikrochim. Acta*, 1961, (2), 314–322 (in German).—Traces of Bi, Cd, Cu, Fe, Ni, Pb and Zn are determined by polarography after removing the Au by extraction with isopropyl ether from 3N-HBr soln. *Procedure*—Dissolve three separate samples (0·5 g) in aqua regia (1 to 2 ml) and evaporate to dryness. Dissolve

each residue in 3N-HBr (5 ml) and extract with isopropyl ether (3 × 10 ml). Evaporate the aq. phase to dryness in a nitrogen atmosphere, add 6N-H_2SO_4 (1 drop) and $HClO_4$ (0·2 ml) and heat to destroy organic matter. Determine Cu, Cd, Ni and Zn on one sample with 6N-aq. NH_3 as basal electrolyte and Bi and Pb on the second sample with 0·5M-Na tartrate at pH 4·5 as basal electrolyte. To the third sample add 6N-H_2SO_4 (1 drop) and 1% hydrazine sulphate soln. (1 drop) and heat gently. Determine Fe polarographically with 0·5M-ammonium tartrate in N-aq. NH_3. The sensitivity is 0·1 to 0·01 p.p.m. and the accuracy ±10 to 20%.

W. T. CARTER

3600. Determination of oxygen in alkaline-earth metals by a distillation method. I. E. D. Malikova and Z. M. Turovtseva. *Trudy Komiss. Anal. Khim., Akad. Nauk SSSR*, 1960, **10**, 103–108; *Ref. Zhur., Khim.*, 1960, (24), Abstr. No. 96,151.—A distillation method can be used to determine O in magnesium and calcium, MgO and CaO being determined in the residue, after distillation of the metal in vacuum, by chemical or spectrographic methods. The chemical method is based on titration of Ca or Mg with EDTA (disodium salt), by the usual method. The sensitivity of the method is dependent on the sensitivity of the titration, by which several micrograms of metal per ml can be determined. Flame photometry, of about the same sensitivity, can also be used to determine these metals in the residue after distillation. The oxygen content of the metal is found by calculation (assuming that the distillation residue is wholly oxide) from the amount of metal found in the residue.

C. D. KOPKIN

3601. Analytical chemistry of beryllium. A review. L. E. Smythe and R. N. Whittem (Australian Atomic Energy Comm. Res. Estab., Sydney, N.S.W.). *Analyst*, 1961, **86**, 83–94.—Methods available for the determination of Be are reviewed. Emission spectrometry can be used for the determination of very small amounts of Be and for health-monitoring purposes, and X-ray techniques for the determination of impurities in beryllium. Mass spectrometry has little application although it has been used for determining gases formed in beryllium by $(n, 2n)$ reactions. Methods for determining impurities in beryllium and its compounds are listed. (159 references.)

A. O. JONES

3602. Gravimetric determination of beryllium with *N*-benzoyl-*N*-phenylhydroxylamine. J. Das and S. C. Shome (Presidency College, Calcutta, India). *Anal. Chim. Acta*, 1961, **24** (1), 37–41 (in English).—Beryllium is pptd. at 50° to 60° and pH 5·5 to 6·5 by ethanolic *N*-benzoyl-*N*-phenylhydroxylamine. The ppt. may be weighed directly or ignited and weighed as the oxide. Results are accurate to within ±2%. Beryllium can be separated quantitatively from Fe, Al and Ti by differential pptn.

A. C. R. HARTLEY

3603. Determination of beryllium with hexaamminecobalt(III) chloride. K. Vetejška (Inst. Res. Ores, Prague). *Sb. Prac. Úst. Pro Výzk. Rud III*, 1958–59, 235–240.—The Be is pptd. as $[Co(NH_3)_6\cdot(H_2O)_2Be_2(CO_3)_2(OH)_2].3H_2O$, which is dissolved in HCl (0·25N to 7N), and the extinction of the soln. is measured at 520 mμ. The method is suitable for the determination of 1 to 12 mg of BeO in 50 ml.

J. ZÝKA

3604. Rapid determination of beryllium. Paper-chromatographic method. D. Ader and A. Alon (Israel Mining Industries Lab., P.O. Box 5249, Haifa, Israel). *Analyst*, 1961, **86**, 125–129.—The finely pulverised sample (20 to 100 mg) is digested and evaporated twice with 40% HF (5 ml). The residue is dissolved in HCl (1:1) and the cooled soln. is adjusted to 25 ml. The chromatographic paper (Whatman No. 1 type CRL/1) is impregnated with a 5% soln. of EDTA (disodium salt) and allowed to dry. The sample soln. (0·01 ml ≡ 0·0002 to 0·3 μg of Be) is applied to the paper, the ends of which are then clipped together to form a cylinder, and the paper is dried in a beaker floating in boiling water. It is then placed in a covered beaker containing 10 to 15 ml of solvent [water - HCl - ethyl methyl ketone (2:3:15) or 5N-HCl - ethanol (1:9)], and when the solvent layer has ascended ≃4 cm the paper is dried in air or as before. It is then exposed to the vapour from aq. NH_3 and sprayed on each side with aq. Eriochrome cyanine R (C.I. Mordant Blue 3) (0·075%). The resulting blue - violet band is compared with those produced with 0·01-ml portions of standard soln. of $BeSO_4$ in dil. HCl chromatographed on the same sheet. Under the conditions described, no interference from other elements occurs.

A. O. JONES

3605. Determination of beryllium by liquid - liquid extraction. D. L. Galkina and A. L. Markman. *Uzbek. Khim. Zhur.*, 1960, (2), 53–65; *Ref. Zhur., Khim.*, 1960, (21), Abstr. No. 84,412.—A method is developed for determining Be in ores after separation from all accompanying metals by extraction of beryllium butyrate with $CHCl_3$ in the presence of EDTA (disodium salt) (**I**). Treat the sample (0·25 to 1 g) with 5 ml of HF, evaporate off the excess of acid, fuse the residue with 4 to 5 g of KHF_2 (first at low temp., and then at 800°), treat the melt with 15 ml of H_2SO_4 (1:1), heat till no more SO_3 is evolved, and fuse at 500° to a clear melt. Treat the melt with water (50 to 60 ml), add 7 to 10 ml of HCl (1:1), heat, and precipitate hydroxides with aq. NH_3. Filter off the ppt., wash it with 2% NH_4Cl soln. (× 2 or 3), dissolve it in the minimum amount of HCl (1:1), evaporate the soln. to 3 or 5 ml and add 5 ml of satd. NaCl soln., 5 to 15 ml of 50% **I** soln. and HCl (1:1) till just acid; heat, cool, adjust the pH of the soln. to between 9 and 10 with aq. NH_3, add 15 ml of butyric acid, heat to boiling, and, after cooling, extract with $CHCl_3$ (2 × 15 ml). Combine the extracts, wash with 10 ml of satd. NaCl soln., containing 3 drops of **I** soln. and 1 drop of 30% H_2O_2, and re-extract the Be with 30 ml of hot HNO_3; to the org. layer add a further 10 ml of conc. HNO_3, mix, add 30 ml of water, again mix, and remove the aq. layer. Combine the aq. extracts, evaporate, make up to 50 ml, and precipitate $Be(OH)_2$ with aq. NH_3. Filter off the ppt., wash it with 2% NH_4NO_3 soln., dissolve it in hot HCl (1:1), and re-precipitate $Be(OH)_2$. Ignite the ppt. to BeO at 800° to 900°, and weigh. The determination can also be completed photometrically with beryllon. There is no interference from Al, Fe, Ti, Sn, Pb, Zr or Cr.

C. D. KOPKIN

3606. Determination of magnesium by atomic absorption flame photometry. [**I.**] W. Leithe and A. Hofer (Hauptlab. der Österreich. Stickstoffwerke Akt.-Ges., Linz). *Mikrochim. Acta*, 1961, (2), 268–276 (in German).—Magnesium can be rapidly determined in limestone, gypsum, anhydrite, cement, slag, plant ash and soil samples by this technique. Samples containing ≃3% of Mg give

results agreeing with those of chemical analysis to within 2%. Aluminium interferes unless Ca^{2+} or SO_4^{2-} are added. Low results are obtained unless the sample soln. has the same acidity as the calibration soln.

II. Determination of magnesium in aluminium alloys. W. Leithe and A. Hofer. *Ibid.*, 1961, (2), 277–282.—Correction for interference from Al in the determination of Mg in aluminium alloys is best achieved by the addition of an equivalent amount of Al to the calibration soln. Since the interference remains substantially the same over the range 0·85 to 1·0 mg of Al per ml, it is possible to analyse alloys containing from 85 to 99·9% of Al with the same calibration. The analysis of 17 alloys of different composition containing 0·2 to 6% of Mg gave results agreeing with those of chemical analysis to within ≃ 5%. W. T. CARTER

3607. **Emission-spectrographic analysis of 65 - 35 and 50 - 50 magnesium - aluminium alloys.** S. Lader (Picatinny Arsenal, Dover, N.J., U.S.A.). *Appl. Spectroscopy*, 1961, **15** (2), 45–46.—The procedure given permits concn. from 0·07 to 1% of Fe, Si, Cr, Pb, Ti, Zn and Sn in the alloy to be determined with a mean coeff. of variation of 5·1%. The sample (0·5 g) is dissolved in conc. HCl and conc. H_2SO_4, 5 mg of Ni is added as internal standard and the soln. is evaporated to dryness. The residue of sulphates is ignited at 600° for 30 min. and mixed with 2 parts of graphite. The mixture is then excited in an a.c. arc (2400 V, 4 amp.) and the spectral lines are recorded (slit-width 30 μ, exposure 40 sec.). The relative transmittance values of the lines are converted into intensity ratios by reference to emulsion calibration curves obtained by a stepped-sector method. W. J. BAKER

3608. **Elimination of phosphate interference in EDTA determinations of calcium and magnesium.** K. R. Middleton (Rubber Res. Inst. of Malaya, P.O. Box 150, Kuala Lumpur, Malaya). *Analyst*, 1961, **86**, 111–116.—To a 25-ml aliquot of the sample soln. (*e.g.*, from plant ash) (≡ ≃ 4 mg of Ca and 1·5 mg of Mg) is added 20 ml of 20% ammonium molybdate soln. followed, after mixing, by 50 ml of NH_4Cl - aq. NH_3 soln. (66 g plus 600 ml in 2·5 litres of water), 1 ml of 3% hydroxylamine soln., 2 ml of 2% KCN soln. and 0·2 g of Eriochrome black T - KCl (1;250). The soln. is then titrated for Ca plus Mg with 0·01M-EDTA (disodium salt). For Mg, a 50-ml aliquot of sample soln. is mixed well with 30 ml of 20% ammonium molybdate soln. and 10 ml of 20% Na_2WO_4 soln., then 10 ml of 50% aq. NH_3 is added and the liquid is heated at 80° to 90° for 30 min. to precipitate Ca. The ppt. is filtered off and washed (× 4) with 2% aq. NH_3. To the combined filtrate and washings are added 15 ml of 50% aq. NH_3, 1 ml of 3% hydroxylamine soln., 2 ml of 2% KCN soln. and 0·2 g of Eriochrome black T - KCl and the soln. is titrated with 0·01M-EDTA, to give a direct measure of the Mg present; the Ca is calculated from the difference between the second titre and twice the first. A. O. JONES

3609. **Determination of calcium in lithium salts.** R. L. Olsen, H. Diehl, P. F. Collins and R. B. Ellestad (Dept. of Chem., Iowa State Univ., Ames, U.S.A.). *Talanta*, 1961, **7** (3–4), 187–194 (in English).—The determination of < 0·0002% of Ca in lithium salts is described. The alkaline soln. containing KOH is either titrated directly with 0·005M-EDTA (disodium salt), with calcein as indicator, or Ca is first separated by adsorption from KOH soln. on Dowex A-1 resin, followed by elution with 2N-HCl. Fluorimetric measurement of the end-point is preferred. Iron (> 0·1%) should be absent. P. D. PARR-RICHARD

3610. **Colorimetric determination of strontium.** R. Palouš, A. Kharnauchoff and S. Mizera (Charles' Univ., Prague). *Anal. Chim. Acta*, 1961, **24** (1), 96–97 (in German).—Dilituric acid (0·05N) is used as a reagent for the colorimetric determination of Sr (up to 2 mg per ml). After 15 min. at room temp. the reaction mixture is filtered, and the extinction is measured at 420 mμ. A number of cations and coloured anions interfere. A. C. R. HARTLEY

3611. **Assay of barium compounds by precipitation of barium chromate from homogeneous solution.** G. Norwitz (Pittman-Dunn Lab., Frankford Arsenal, Philadelphia, Pa., U.S.A.). *Anal. Chem.*, 1961, **33** (2), 312–313.—The time required for the pptn. of $BaCrO_4$ in homogeneous soln. at controlled pH by the method of Gordon and Firsching (*cf. Anal. Abstr.*, 1954, **1**, 1785) can be considerably reduced by the addition of conc. HCl (7 ml), or $HClO_4$ (6 ml) plus conc. HCl (2 ml), and boiling the soln. (≃ 230 ml), first until a ppt. appears (≃ 15 min.) and then for a further 60 min. During boiling the pH remains constant at 5·5, and carbonate, sulphide and peroxide are destroyed. If F^-, Si or organic anions are present, the soln. must be heated to fuming with $HClO_4$ before dilution. If > 3% of a strontium compound is present, a double pptn. is necessary. W. J. BAKER

3612. **Separation of radioactive zinc from reactor cooling-water by an isotope-exchange method.** W. B. Silker (General Electric Co., Richland, Wash., U.S.A.). *Anal. Chem.*, 1961, **33** (2), 233–235.—High yields of ^{65}Zn, free from all other activities except those of ^{64}Cu and ^{56}Mn, are obtained by allowing the sample (100 ml adjusted to 0·1M in tartaric acid) to remain in contact with zinc amalgam for ≃ 8 min., separating the amalgam, and counting on a γ-ray spectrometer. Recoveries average 98·9%, with a standard deviation of 4·7%, of which 2·5% is ascribed to counting. The error caused by ^{56}Mn is only ≃ 2% but, if high accuracy or radiochemically pure ^{65}Zn or ^{69m}Zn is required, ^{64}Cu must be removed quant. by pre-extraction into cadmium amalgam. W. J. BAKER

3613. **Solvent-extraction method for the radiochemical determination of zinc [in reactor cooling-water].** W. J. Maeck, M. E. Kussy and J. E. Rein (Atomic Energy Div., Phillips Petroleum Co., Idaho Falls, U.S.A.). *Anal. Chem.*, 1961, **33** (2), 235–236.—After oxidation and pptn. of Ru with 0·05M-Ce^{4+} in N-$HClO_4$, most of the remaining interfering ions that form insol. hydroxides are pptd. with 10N-NaOH at pH 14. The amphoteric Zn (plus Al, which does not interfere) is then pptd. from the filtrate at pH 8·2, the ppt. is dissolved in aq. NH_3, and the complex of Zn with diethyldithiocarbamate is formed and extracted into ethyl acetate. The complex is re-extracted into 0·2N-HCl, and the Zn is determined by titration with EDTA at pH 9·5 (for yield, usually ≃ 60%) and by counting in a well-type NaI(Tl) scintillation crystal. The fission yield of ^{72}Zn in irradiated ^{235}U was $2·6 \times 10^{-3}$ % by this method; the error is ≃ 10%. W. J. BAKER

3614. **Rapid determination of aluminium, iron, copper, cadmium and lead in zinc-base alloys.** R. J. Gajan and D. M. Geehan (College Park Metall. Res. Center, Md., U.S.A.). *Rep. Invest. U.S. Bur. Min.*, 1961, No. 5727. 10 pp.—After dissolution of the sample in HCl (sp. gr. 1·19), aliquots are taken for spectrophotometric determinations of Al, with aluminon, and of Fe, with 1,10-phenanthroline. A further aliquot is polarographed for Cu, Cd and Pb. Comparative results on N.B.S. standard alloys are given. G. P. MITCHELL

3615. **Ultra-violet spectrophotometric determination of traces of lead, iron and copper in zinc sulphate.** M. J. Maurice and S. M. Ploeger (Zentral. Forschungsinst. d. A.K.U. u. Konzerngesellschaften, Arnhem, Netherlands). *Z. anal. Chem.*, 1961, **179** (4), 246–258 (in German).—Iron and Cu in 6N-HCl may be determined by direct measurement of the extinctions at 278 mμ and 360 mμ: Fe (mg per 100 ml) = $2{\cdot}046E_{360}-0{\cdot}311E_{278}$, and Cu (mg per 100 ml) = $2{\cdot}122E_{278}-1{\cdot}754E_{360}$. Lead must be removed and determined separately. *Procedure*—Dissolve the sample in water (40 ml), cool, add conc. H_2SO_4 (15 ml), set aside for 4 hr. and centrifuge. Dissolve the pptd. $PbSO_4$ in 5M-ammonium acetate (5 ml), add 12N-HCl (50 ml), dilute to 100 ml and measure the extinction at 270 mμ against a blank. Determine the Pb from a standard curve. Dilute the supernatant liquid from the $PbSO_4$ ppt. to 100 ml. To 50 ml add 12N-HCl (50 ml) and measure the extinctions at 278 mμ and 360 mμ. Extinctions are corrected for the absorption due to $ZnSO_4$ and organic impurities; E_{278} is corrected for the Pb remaining in soln., and for Sb if $>1\times10^{-4}$% is present. At concn. $<3{\cdot}5\times10^{-4}$% of Fe and $<0{\cdot}2\times10^{-4}$% of Cu the results are unreliable. The method is rapid and the results agree with those by the sulphosalicylic acid and diethyldithiocarbamate methods for Fe and Cu, respectively. A. J. BENNETT

3616. **Quantitative determination of cadmium by the direct oxidimetric titration of sulphide ion.** A. G. Kankanyan and R. G. Meloyan. *Izv. Akad. Nauk ArmSSR, Khim. Nauk*, 1959, **12** (4), 261–265; *Ref. Zhur., Khim.*, 1960, (20), Abstr. No. 80,763.—The method is based on the separation of Cd as CdS, and the titration of S^{2-} with chloramine T (**I**) soln. in a neutral or acid medium. The oxidation potential of **I** is 0·9 V in neutral medium, and 1·52 V in acid medium. The pptn. of Cd is carried out in ammoniacal medium with thiourea. The ppt. is washed with hot water and returned with the filter to the pptn. vessel; 20 ml of water, 2 g of KI and 2 ml of starch soln. are added, and the soln. is titrated with **I** soln. to a stable blue colour. The soln. of **I** is standardised iodimetrically. In acid medium (acetic acid) the reaction is much more rapid, and the error is $>0{\cdot}35$%. The use of $KBrO_3$ for the direct titration of S^{2-} was not satisfactory. C. D. KOPKIN

3617. **Neutron-activation method for the determination of traces of cadmium in aluminium.** E. Ricci and W. D. Mackintosh (Chem. and Metall. Div., Atomic Energy of Canada Ltd., Chalk River, Ontario). *Anal. Chem.*, 1961, **33** (2), 230–233.—A simple and sensitive method is described for the determination of Cd at the 1 in 10^9 level. Simultaneous irradiations of samples and comparative standards are carried out, the induced radioactivity from the cadmium impurity is separated from the matrix by ion exchange on Dowex 1-X8 (100 to 200 mesh, Cl^- form), purified by pptn. and then counted. It is estimated that 10^{-10} g of Cd in a 0·5-g sample of aluminium would yield a suitable peak for measurement on a γ-ray spectrometer. The relative standard deviation is ± 9·4%. C. B. BAINES

3618. **Application of complexans in chemical analysis. LIV. Polarographic determination of cadmium in metallic indium.** M. Kopanica and R. Přibil (Inst. of Geochem. and Raw Material Res., Czech. Acad. Sci., Prague). *Coll. Czech. Chem. Commun.*, 1961, **26** (2), 398–402 (in English).—In the polarographic determination of cadmium impurities in indium, the In is masked by 1,2-diaminocyclohexane-*NNN'N'*-tetra-acetic acid (**I**), and the Cd is quant. displaced at pH 2·7 to 3·5 from its complex (stability const., log K = 19·23) by $Th(NO_3)_4$, with xylenol orange as indicator. Similarly Pb and Tl, and also Zn, Ni and Co, are displaced by Th, but the latter group of metals cannot be determined polarographically in this medium. *Procedure*—Dissolve the indium (0·5 g) in the minimum amount of $HClO_4$ and evaporate the soln. almost to dryness. Dissolve the residue in H_2O (10 ml), add a few drops of aq. NH_3 (1:1) and then formate buffer (pH 3) (20 ml) and 0·5M-**I** (20 ml). Add 1% xylenol orange soln. (1 drop) and then, dropwise, 10% $Th(NO_3)_4$ soln. to a permanent red colour. Dilute to 50 ml and record the polarogram from − 0·2 to − 1·0 V *vs.* the S.C.E. The $E_{\frac{1}{2}}$ of Cd is at − 0·60 V. J. P. STERN

3619. **Improved volumetric determination of boric acid by means of a pH paradox.** F. L. Hahn (Angel Urraza 718–303, México 12, D.F., México). *Anal. Chem.*, 1961, **33** (2), 316–317.—An example of a pH paradox is the lowering, instead of the raising, of the pH when an alkaline reagent is added to another buffered soln. of different pH. This effect is utilised in the usual titration of H_3BO_3 or borates by adding a mixed soln. containing ≃60% of sorbitol and 0·1N in NaOH, which first transforms the acid being titrated and then measures it. A soln. of borate can be titrated first with acid and then with the sorbitol - 0·1N-NaOH. The end-point is located by interpolation on the potentiometric curve (*cf. Anal. Abstr.*, 1958, **5**, 3975). W. J. BAKER

3620. **Sodium tetraborate (borax). Photographic grade.** British Standards Institution (2 Park Street, London, W.1). B.S. 3311 : 1961. 8 pp.—Tests for purity and a method of assay are included.

3621. **Homogeneous precipitation of aluminium 8-hydroxyquinolinate.** L. C. Howick and W. W. Trigg (Dept. of Chem., State Univ., Fayetteville, Ark., U.S.A.). *Anal. Chem.*, 1961, **33** (2), 302–303.—Quant. homogeneous pptn. of dense crystalline Al 8-hydroxyquinolinate can be made by hydrolysis of 8-acetoxyquinoline (**I**) at pH 5 and 60°. *Procedure*—To the slightly acid sample soln. (50 ml ≡ 5 to 22 mg of Al) add a soln. of **I** (7 g) in 4N-acetic acid (35 ml) and heat the mixture on a water bath at 60° for 5 hr. Collect the ppt. on a weighed filter-disc, wash twice with H_2O, dry at 125° for 3 hr. and weigh. The mean error is ≃ −0·25%, and a max. of 30% of Cd can be tolerated in the sample. The

preparation of a stable mixture of **I** by a modification of Dimroth's method (*Annalen*, 1926, **446**, 119) is described. W. J. BAKER

3622. **Fluorimetric analysis. XII. Determination of aluminium by extraction of its Pontachrome blue black R complex with amyl alcohol and its application to the analysis of pure magnesium.** Masayoshi Ishibashi, Tsunenobu Shigematsu and Yasuharu Nishikawa (Inst. Chem. Res., Kyoto Univ., Sakyo-ku). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1960, **81** (2), 259–262.—In order to eliminate the quenching action of foreign ions, the Pontachrome blue black R (C.I. Mordant Black 17) (**I**) complex of Al is extracted with amyl alcohol from an ammonium acetate buffer of pH 4·8. The optimum amount of **I** is 0·2 ml of 0·1% soln. per 50 ml of aq. soln. Interference results from UO_2^{2+} and Ni (in > 10-fold excess), Cu, Co, Ti and Ga; Fe^{III} and VO_3^- must be reduced with hydroxyammonium chloride. *Procedure for Al in metallic magnesium*—Dissolve the sample (0·1 g) in H_2SO_4 (1:9) (4 ml) and make up to 100 ml. Treat an aliquot containing 0·05 to 1·5 μg of Al with **I**, ammonium acetate soln. (10%) (5 ml) and water (total ≃ 50 ml), adjust the pH to 4·8 with aq. NH_3 soln. and H_2SO_4, heat on a water bath for 10 min. and extract with amyl alcohol (25 ml). Measure the fluorescence at ≃600 mμ, with rhodamine B (C.I. Basic Violet 10) soln. (0·3 μg per ml) as reference. K. SAITO

3623. **Spectrographic analysis of aluminium and nickel alloys.** A. S. Dem'yanchuk and O. P. Ryabushko. *Inzh.-Fiz. Zhur.*, 1960, **3** (4), 111–114; *Ref. Zhur., Khim.*, 1960, (20), Abstr. No. 80,848.—A method is described for the analysis of primary aluminium, silumins, Al - Mg alloys, duralumin and V-95 alloys with one set of standards. The spectra are excited in a h.f. spark discharge with a primary transformer winding current of 0·8 amp. and a potential in the secondary winding of 4000 V. The secondary gap is 1·0 mm long and the working gap 1·8 mm, with a preliminary sparking for 40 sec. and exposure for 30 sec. The spectra are excited with a carbon electrode sharpened to a cone and photographed in a medium spectrograph. Calibration curves are constructed with Fe 2611·9, Si 2516·1 and 2435·2, Mg 2779·8, Ni 2416·1, Cr 2677·2 and Zn 2502·0 A, with Al 2660·4 A as comparison line, and Ca 3179·3, Mn 2949·2, Cu 3274·0 and Ti 3349·4 A, with Al 3064·3 A as comparison line. The minimum determinable concn. of impurities is 0·01 to 0·02%. In the analysis of nickel alloys, the spectra are excited in a high-voltage spark discharge with a copper electrode sharpened to a cylinder of diam. 0·8 mm, and photographed with a 0·005-mm slit on Type II plates with triple-lens illumination and preliminary sparking for 1 min. The analysis is carried out with the lines B 2496·8, Fe 2599·4, Si 2528·5 and Mn 2593·7 A, with Ni 2584·0 A as comparison line; and Al 3082·2, Ti 3075·2 and Cr 3147·2 A, with Ni 3080·8 A as comparison line. The error of the determination is ⩾4%. C. D. KOPKIN

3624. **Detection of gallium after preliminary concentration.** V. K. Kuznetsov and N. A. Tananaev. *Trudy Ural'sk. Politekh. Inst.*, 1960, (94), 145–148; *Ref. Zhur., Khim.*, 1960, (21), Abstr. No. 84,428.—A method for detecting Ga in the presence of Al, Zn, In, Cr, Ti, V, Pb, Mg, Co, Ni, Tl, Ag and Cd is described. *Procedure*—To the test soln. add a fresh suspension of $Al(OH)_3$, prepared by adding an excess of an Al salt to 1% NaOH soln., stir the mixture well with slight heating, filter off the ppt., wash it, and dissolve it in 2 to 3 ml of 10% NaOH soln. To the resulting soln. add ammonium oxalate to saturation, 2 to 3 drops of ethanolic alizarin soln. and 1·5 to 2 ml of ethyl ether. After shaking the mixture the gallium lake collects as crimson flocks or films at the interface. At pH 8 to 9 the ether layer is colourless. To accelerate the separation of the layers, add 1 or 2 drops of ethanol. In the presence of large amounts of Fe^{3+}, first reduce these to Fe^{2+}. The sensitivity of the reaction is 1×10^{-6} g of Ga per ml. C. D. KOPKIN

3625. **Determination of gallium with C-cyano-*NN'*-di-(2-hydroxy-5-sulphophenyl)formazan.** N. L. Vasil'eva, M. I. Ermakova and I. Ya. Postovskii. *Zhur. Vses. Khim. Obshch.*, 1960, **5** (1), 110; *Ref. Zhur., Khim.*, 1960, (21), Abstr. No. 84,429.—It is shown that, in the presence of Ga, *C*-cyano-*NN'*-di-(2-hydroxy-5-sulphophenyl)formazan (**I**) acquires a blue colour. At pH 3 and wavelength 600 to 656 mμ, Beer's law is obeyed for concn. of Ga from 0·035 to 0·35 μg per ml. Aluminium reacts with **I** only at pH ⩽ 4 and does not interfere. A photometric method for determining Ga (< 0·001%) in aluminium is developed on this basis. *Procedure*—Dissolve the sample (0·01 to 0·05 g) by heating with HCl (1:1), evaporate to a small vol., dilute with M-Na acetate to 15 ml, adjust the pH to 3, make up to 20 ml with acetate buffer soln. (pH 3), add 1 ml of 0·1% aq. **I** soln., set aside for ≃12 hr., and measure the extinction with a red filter, and a soln. of the same composition, but without Ga, as comparison soln. Copper, Fe, Co, V and Ti interfere. The synthesis of **I** is described. C. D. KOPKIN

3626. **Quantitative determination of gallium in micro samples by the graphite spark.** E. M. Murt and J. C. Bready (Philco Corp., Lansdale Div., Lansdale, Pa., U.S.A.). *Appl. Spectroscopy*, 1961, **15** (1), 1–3.—Micro samples (<0·1 mg) of an In - Ga alloy are dissolved in sufficient 8N-HCl to give a final soln. 1N to 2N in HCl and containing 0·10 mg of alloy per ml. Each of two flat-ended graphite electrodes (0·18 in. in diam.) is loaded with 2 drops of Apiezon N - light petroleum soln., 0·05 ml of standard ammonium molybdate soln., containing 0·005 mg of Mo per ml, and 0·05 ml of the test soln., and the electrodes are allowed to dry under an i.r. lamp before use. The electrodes are sparked together for each spectrum, which is recorded on a Bausch and Lomb large Littrow spectrograph set for the range 2490 to 3470 A. A linear working curve was obtained by measuring Ga 2874·2 A, with Mo 2879 A as internal standard and a range of synthetic standard soln. corresponding to concn. of Ga between 0·1 and 1·2%. From a calculation of the coeff. of variation, the accuracy of the method is estimated to be within the range of ± 11% at the 1·0% level of Ga to ± 22% at the 0·2% level. P. T. BEALE

3627. **Fluorescence analysis of inorganic substances. I. Study of the fluorescence reaction of gallium with Rhodamines S and 6G.** D. P. Shcherbov, I. T. Solov'yan, A. I. Ivankova and A. V. Drobachenko. *Trudy Kazakh. Nauch.-Issled. Inst. Mineral. Syr'ya*, 1959, (1), 188–195; *Ref. Zhur., Khim.*, 1960, (20), Abstr. No. 80,767.—A study is made of the suitability of a number of dyes for the fluorimetric detection and determination of Ga.

Rhodamine S (C.I. Basic Red 11) (**I**) is a more selective reagent for Ga than Rhodamine 6G (C.I. Basic Red 1), but Y, Au, Tl, Sb and Te interfere in the determination of Ga with **I**. The interference of most of these elements can be avoided by reducing them to a lower valency state with $TiCl_3$. The following method for the determination of Ga in ores is proposed. Dissolve the sample in HCl (1:1), add $TiCl_3$ and a soln. of **I** in HCl, and extract with benzene - ethyl ether (9:1). By irradiating with a fluorescent lamp, 0·05 to 2 μg of Ga can be determined in 3 ml of extract. This allows about 10^{-4} % of Ga to be determined with a discrepancy between parallel analyses of 0·0002 to 0·0003%.

II. Fluorimetric determination of gallium in ores using Rhodamine S. D. P. Shcherbov and I. T. Solov'yan. *Trudy Kazakh. Nauch.-Issled. Inst. Mineral. Syr'ya*, 1959, (1), 196–199; *Ref. Zhur., Khim.*, 1960, (20), Abstr. No. 80,767.—Details of methods for the decomposition of the sample and of the measurement of the fluorescence are given.

C. D. Kopkin

3628. **Separation of gallium from copper and nickel by ion exchange.** E. P. Tsintsevich and A. N. Gorokhova. *Izv. Vyssh. Uchebn. Zavedenii, Khim. i Khim. Tekhnol.*, 1960, **3** (2), 245–250; *Ref. Zhur., Khim.*, 1960, (23), Abstr. No. 92,005.—The method is based on the selective adsorption by resin EDE-10P of the anionic complexes of Ga formed in the presence of ammonium carbonate and aq. NH_3. At ammonium carbonate concn. >0·3M, resin KU-2 (NH_4^+ form) hardly adsorbs Ga, while EDE-10P (CO_3^{2-} form) quant. retains it. In the presence of ammonium carbonate, Ni forms a cationic complex if aq. NH_3 (1:1) is added to the soln. until the colour changes from blue - green to blue - violet. To obtain the corresponding ammoniacal complex of Cu, to 4 mg of Cu add 2M-ammonium carbonate till the ppt. dissolves and dilute with aq. NH_3 (1:1) to 200 ml. Under these conditions Ga is quant. separated from Ni and from Cu with Ga to Ni and Ga to Cu ratios of from 1:1 to 1:10,000. Copper is determined iodimetrically in the percolate from the column, and Ni by titration with 0·02N-dimethylglyoxime. Gallium is eluted from the column with 2·5N-HCl, and the eluate is boiled to remove CO_2 and used for the photometric determination of Ga as the complex with gallion at pH 2·4 to 3·2, with a filter having max. transmission at 610 mμ. The colour of the complex is stable for >40 hr.

C. D. Kopkin

3629. **Determination of the number of electrons taking part in the reduction of indium on the dropping-mercury electrode.** P. K. Agasyan, E. N. Vinogradova and Ching-Ju An (M. V. Lomonosov Moscow State Univ.). *Zavod. Lab.*, 1961, **27** (2), 131–135.—By means of a micro-coulometric method the number of electrons taking part in the reduction of In in the presence of $HClO_4$, succinic acid and trihydroxyglutaric acid is found to be 2 in all cases.

G. S. Smith

3630. **Extraction and radiometric determination of indium.** I. M. Korenman, F. R. Sheyanova, T. N. Mitrokhina and T. N. Trapeznikova. *Trudy Khim. i Khim. Tekhnol.*, 1959, (2), 414–420; *Ref. Zhur., Khim.*, 1960, (20), Abstr. No. 80,768.—The extraction of In dithizonate and 8-hydroxyquinolinate with $CHCl_3$ is studied in relation to the pH of the soln. The dithizonate is completely extracted at a pH of ≃5, and the 8-hydroxyquinolinate at pH ≃4. A method is developed for the radiometric titration of 10 to 100 μg of In. *Procedure*—Place 2 ml of test soln. (containing ^{115}In) of the required pH in each of several tubes, add $CHCl_3$ and various amounts of 0·002M-dithizone (or 0·005M-8-hydroxyquinoline) in $CHCl_3$ to a total organic phase of 2 ml, shake for 15 min. and centrifuge. Measure the activities of 0·5-ml samples of the aq. and org. phases, and construct the titration curves, *i.e.*, the relationship between the activities of the phases and the dithizone (or 8-hydroxyquinoline) added. The extractant soln. are standardised against soln. of In. The method can be used for determining In in the presence of Zn, Ga, Cd and Tl. The error is ≯ 8%.

C. D. Kopkin

3631. **Spectrophotometric determination of indium in zinc and zinc oxide.** T. A. Collins, jun., and J. H. Kanzelmeyer (Zinc Smelting Div., St Joseph Lead Co., Monaca, Pa., U.S.A.). *Anal. Chem.*, 1961, **33** (2), 245–247.—From 2 to 100 μg of In in the sample (after dissolution and evaporation with conc. HCl plus 70% $HClO_4$) can be determined by first extracting the In into isopropyl ether from 6N-HBr, re-extracting it into H_2O, then extracting it from the aq. soln. (adjusted to pH 9 with hydroxy-ammonium chloride and KCN) into 0·002% dithizone soln. in $CHCl_3$, and finally measuring the extinction of the organic phase at 510 mμ in a 1-cm borosilicate cell. Beer's law is followed and the accuracy is within 2·6% for concn. from 0·0007 to 0·01% of In. Interferences and their control are discussed; large amounts of Fe (as in drosses, concentrates and residues) must be removed initially.

W. J. Baker

3632. **Determination of thallium in its alloys with antimony, arsenic or phosphorus.** A. I. Busev and V. G. Tiptsova. *Izv. Vyssh. Ucheb. Zavedenii, Khim. i Khim. Tekhnol.*, 1960, **3** (1), 69–71; *Ref. Zhur., Khim.*, 1960, (20), Abstr. No. 80,770.—Gravimetric and titrimetric methods are described for the determination of Tl in its alloys with Sb and also in the presence of As and P, after separation of Tl as diantipyrinylmethane tetrabromothallate ($C_{23}H_{24}O_2N_4.HTlBr_4$) (**I**) (*Anal. Abstr.*, 1960, **7**, 56). Antimony as the tartrate complex is not pptd. by diantipyrinylmethane (**II**) in the presence of Cl^- and Br^-, and PO_4^{3-} and AsO_4^{3-} are not pptd. by it from acid soln. In the gravimetric determination, Tl^+ are converted into $TlBr_4^-$ by successively adding soln. of HBr and $KBrO_3$, excess of Br is removed with sulphosalicylic acid, tartaric acid is added, and $TlBr_4^-$ are pptd. as **I** by adding **II**. In the titrimetric determination, freshly pptd. **I** is dissolved in a standard soln. of EDTA (disodium salt) at pH 8, and the excess of the EDTA is titrated with Zn acetate soln., to Eriochrome black T. The titrimetric method is particularly suitable for small amounts of Tl. These methods have been tested on synthetic mixtures containing various amounts of Sb^{3+}, Na_2HPO_4 and Na_2AsO_4. In determining 5·35 to 10·7 mg of Tl in the presence of Sb (the Tl:Sb ratio varying from 2:1 to 1:100) the max. error was ≃ 0·3 mg of Tl. The error was approx. the same when determining analogous amounts of Tl in the presence of P and As, and when using the titrimetric variant of the method.

C. D. Kopkin

3633. **Comparative accuracy of some gravimetric methods for the determination of cerium.** S. A. Gusinskaya. *Izv. Vyssh. Ucheb. Zavedenii, Chern. Metallurg.*, 1960, (3), 193–197; *Ref. Zhur., Khim.*, 1960, (21), Abstr. No. 84,435.—The accuracies of

various gravimetric semi-micro methods for determining Ce are compared by means of the isotope ^{142}Ce. In determining 11·96 mg of Ce, the losses by solubility are (in %): 0·4 to 1·4 (iodate method), 0·9 to 1·9 (oxalate method), 0·3 to 1·3 (hydrate method) and 1·8 to 2·8 (8-hydroxyquinoline method). The oxalate method can be used successfully to separate Ce from Mn, Cr and Fe, but not from Ni. The iodate method gives a good separation of Ce from Ni. To determine Ce in the presence of Fe, Ni, Mn, Cr and Ti, to 10 to 15 ml of a soln. of the alloy (5 to 10 mg of Ce) add 5 to 8 ml of conc. HNO_3, oxidise Ce by slight heating with 0·2 to 0·3 g of $KBrO_3$, and precipitate with a 10-fold excess of KIO_3 (100 g of KIO_3 and 333 g of conc. HNO_3 in 1 litre of soln.). Filter after 3 hr. and wash (× 3) with a soln. containing 0·8 g of KIO_3 and 5 ml of conc. HNO_3 in 100 ml. To the ppt. and filter, add 10% oxalic acid soln. in excess, and boil to remove the iodine formed by reduction of the iodate. Set the soln. aside for 3 hr. Filter off the oxalate ppt. on paper pulp, wash it (× 3 or 4) with hot 1% oxalic acid soln., ignite, and weigh as CeO_2.

C. D. KOPKIN

3634. **Spectrophotometric determination of microgram amounts of cerium.** F. Culkin and J. P. Riley (Dept. of Oceanography, Univ., Liverpool, England). *Anal. Chim. Acta*, 1961, **24** (2), 167–170 (in English).—The red ferrous - 1,10-phenanthroline complex is oxidized by Ce^{IV}, and the resulting diminution in colour intensity provides a measure of the amount of Ce present. *Procedure*—To a 4-ml aliquot of sample soln. (containing $\geq$80 μg of Ce and of acidity $\geq$0·1N) add 0·13 ml of conc. H_2SO_4, 0·5 ml of aq. Ag_2SO_4 (0·1445 g per litre) and 1 ml of 2% aq. $(NH_4)_2S_2O_8$ soln. Heat in a boiling-water bath for 10 min., cool, and add 1 ml of a soln. of 1 g of 1,10-phenanthroline and 0·0653 g of $(NH_4)_2SO_4.FeSO_4.6H_2O$ in 250 ml of 0·1N-H_2SO_4. Buffer the soln. at pH 2·3 with 1 ml of 4·5M-Na acetate and dilute to 10 ml. Measure the extinction within 30 min. at 510 mμ in a 1-cm cell. Refer results to a calibration curve. Of the common metals only Cr, Mn and V interfere. Oxalate, citrate, tartrate, Cl^-, F^- and ClO_4^- must be removed by fuming with H_2SO_4. H. N. S.

3635. **Precise difference-method for the spectrophotometric determination of cerium(IV) at micromolar concentrations.** L. A. Blatz (Sci. Lab., Univ. of Calif., Los Alamos, N.M., U.S.A.). *Anal. Chem.*, 1961, **33** (2), 249–252.—Concn. of Ce from 5 to 12 × 10^{-6}M can be determined, with high reproducibility and precision, by modifying the method of Medalia and Byrne (*Anal. Chem.*, 1951, **23**, 453) to permit the extinctions of the sample soln. at 320, 340 and 360 mμ to be measured in 10-cm silica cells before and after reduction of Ce^{4+} to Ce^{3+} with dil. H_2O_2. Any organic matter present, *e.g.*, cation-exchange resin, must be destroyed by boiling the soln. for 10 to 15 min. with $(NH_4)_2S_2O_8$; the ice-cooled soln. is then filtered through a fine-pore disc before reading the extinctions. Beer's law is followed, and the probable error for a single sample is ≃0·25% at each wavelength. Iron, Th, U, Nd, Zr, NO_3^- and excess of $S_2O_8^{2-}$ do not interfere; other possible interferences and operating factors influencing precision are discussed.

W. J. BAKER

3636. **Determination of small amounts of rare-earth elements in bismuth.** D. I. Ryabchikov and V. K. Belyaeva. *Trudy Komiss. Anal. Khim., Akad. Nauk SSSR*, 1960, (12), 217–220; *Ref. Zhur., Khim.*, 1960, (22), Abstr. No. 88,291.—*Procedure*—Dissolve bismuth (3 g) in conc. HNO_3 (10 to 20 ml), add spectrographically pure Nd (1 mg) as the carrier and ^{91}Y as the radioactive indicator, cool and dilute to 200 ml. Electrolyse the soln. in a platinum dish, which serves as the cathode, at 3 V and 2 amp. with a platinum-wire anode. Repeat the electrolysis at 0·5 to 0·6 V with a Fisher cathode and platinum-wire anode. To complete the separation of Bi, precipitate the lead impurity as sulphide in moderately acid (HNO_3) medium. Evaporate the soln. almost to dryness, dissolve the residue in H_2O (1 to 2 ml) and precipitate the rare-earth-metal hydroxides with aq. NH_3. Measurement of the activity of the ppt. shows that 85% of the rare-earth elements originally present are recovered. The results of X-ray analysis are in good agreement with those of radiochemical determinations. The method can be used to determine 1 p.p.m. of rare-earth elements in high-purity bismuth.

K. R. COOK

3637. **Colorimetric determination of praseodymium.** M. N. Ambrozhiĭ and L. I. Shlȳchkova. *Uch. Zap. Saratovsk. Univ.*, 1959, **71**, 65–68; *Ref. Zhur., Khim.*, 1960, (21), Abstr. No. 84,436.—The photometric determination of Pr in the presence of Nd (0·1 to 1·0% of Pr) is based on the reaction of PrO_2 with *o*-tolidine (**I**) in acetic acid medium (pH 4). Salts of the rare-earth elements (nitrates, oxalates or carbonates) are first decomposed by heating to 900°, to form PrO_2, CeO_2 and the rare-earth-element sesquioxides, but CeO_2 is insol. in acetic acid and therefore does not interfere in the determination of Pr. To determine Pr, add to a sample of the oxide, acetate buffer soln. (pH 4) and a soln. of **I** (dissolve 0·02 g of **I** by heating with 1 ml of 60% acetic acid and dilute to 2 ml with N-acetic acid; if a turbidity forms, add a few drops of acetone), centrifuge the resulting mixture for 10 min. (2000 to 2500 r.p.m.), and after 8 to 10 min. measure the extinction of the soln. with a green filter. Beer's law is obeyed for 0·01 to 1% of Pr (in mixtures with Nd). The colour is stable for ≃40 min. The oxides of Ce and the rare-earth elements of the Ce sub-group do not interfere; MnO_2, PbO_2, and other oxides giving an analogous reaction with **I** in acetic acid medium interfere. The method is applied to the determination of Pr in rare-earth-element oxides obtained from monazite, chevkinite and eschynite. C. D. KOPKIN

3638. **Determination of samarium and other rare-earth metals.** L. R. Pitwell (Dominion Magnesium Ltd., Haley, Ontario, Canada). *Analyst*, 1961, **86**, 137–140.—Methods for the determination of Sm are summarised with an indication of their limitations, and a spectrographic procedure is described for use with typical alloys. Samarium lines in the region 2000 to 4350 A and some in the visible region are listed, with observations on their suitability, a d.c. arc source and an aluminium carrier being used. For small amounts of Sm, La provides a suitable internal standard because it has a relatively simple spectrum, occurs naturally with Sm, has similar chemical properties in the tervalent state and gives satisfactory working graphs. The separations and procedures outlined were applied to mixtures containing known amounts of rare-earth metals together with Th, Zr, Ca and Mg. Satisfactory recovery was obtained with typical soln. A. O. JONES

3639. Spectroscopic determination of the isotopic composition of carbon. A. N. Zaidel and G. V. Ostrovskaya. *Optics and Spectroscopy*, 1960, **9** (2), 78–80; English translation of *Optika i Spektroskopiya*, 1960, **9**, 142–147.—A water-cooled capillary discharge tube, in which the spectrum is excited by an electrodeless h.f. discharge, is used for the determination of the isotopic composition of C, introduced into the tube as CH_4. Admixture of O with the CH_4 prevents the deposition of C on the tube walls and enhances the CO spectrum (Ångstrom bands). The ^{12}CO band at 4123·6 A is used in the analysis, the corresponding band of ^{13}CO being displaced 8·2 A towards the red. The coeff. of variation was 5 to 7% for ^{13}C contents between 1% and 5%, and 2 to 3% for ^{13}C contents between 5% and 60%. The gas consumption was 0·1 to 0·2 ml and the time required for each determination was 10 to 15 min. B. S. COOPER

3640. Determination of very small amounts of carbon dioxide and the analytical application of the methods. E. Schulek, J. Trompler, A. Endrői-Havas and I. Remport (Inst. Inorg. and Anal. Chem., L. Eötvös Univ., Budapest). *Anal. Chim. Acta*, 1961, **24** (1), 11–19 (in German).—Carbon dioxide is absorbed in excess of $Ba(OH)_2$ soln. (0·1N or 0·01N) which is protected from atmospheric CO_2 by a layer of pentane. The soln. is then titrated, with phenolphthalein as indicator for the 0·1N soln. and α-naphtholphthalein for the 0·01N soln. Results are accurate to within 1%. The method is applicable to the determination of C in organic compounds. The apparatus is illustrated. A. C. R. HARTLEY

3641. Indirect complexometric titration of thiocyanate ions with EDTA. R. Ralea and E. Simininuc. *An. Ştiinţ. Univ. "Al. I. Cuza," Iaşi, Sect. I.*, 1960, **6** (1), 171–174.—To a sample containing 1 to 6 mg of SCN^- add a measured excess of 0·01M-Cu^{2+} soln. Make up to 50 ml with H_2O and pass SO_2 for several minutes. Filter through a sintered glass filter and wash the ppt. with 100 ml of H_2O. To the filtrate and washings add 2 ml of M-aq. NH_3 and 2·5 ml of M-NH_4Cl, then 0·04 g of murexide (1% in solid NaCl), and titrate the excess of Cu with 0·01M-EDTA. Iodine, CN^-, Ni, Co, Zn and Cd interfere, but Cl, Br and alkaline-earth metals do not. D. R. DUNCAN

3642. Simultaneous determination of germanium and gallium in coal and volatile products of electric power stations. E. Urbánek (Centr. Lab. of Coal Mines, Zbůch, Czechoslovakia). *Paliva*, 1961, **41** (3), 88–91.—*Procedure with coal*—Decompose the sample (1 to 2 g) (which may first have been ignited at 500° to 550° in a stream of O) with a mixture of H_2SO_4 and HNO_3, and remove silicic acid by repeated evaporation with HF. Transfer the residue with 25 to 30 ml of H_2O to a distillation flask, add an equal vol. of conc. HCl and distil off $GeCl_4$ in a stream of CO_2. Dilute the distillate with H_2O to 50 ml (the final concn. of HCl is 3N). Dilute a 5 to 10-ml aliquot of this soln. with H_2O till the concn. of HCl is 1·2 to 1·5N, add H_2SO_3 soln. (5%) (2 ml), gelatin soln. (0·5%) (2 ml) and phenylfluorone soln. [0·2 g dissolved in 850 ml of 96% ethanol and 50 ml of H_2SO_4 (1:6) and diluted with ethanol to 1 litre] (5 ml), dilute with 1·2N to 1·5N-HCl to 50 ml and after 30 to 60 min. measure the extinction at 510 mμ (for Ge). Dilute the residue in the distillation flask to 50 ml with 6N-HCl and determine Ga in an aliquot photometrically, with Rhodamine B or malachite green as reagent after, extraction into benzene - ether or benzene, respectively. The influence of Fe^{III}, Sb^V and Tl^{III} is overcome by the addition of $TiCl_3$. J. ZÝKA

3643. Determination of traces of oxygen in germanium. A. K. Babko, A. I. Volkova and O. F. Drako. *Trudy Komiss. Anal. Khim., Akad. Nauk SSSR*, 1960, **12**, 53–64; *Ref. Zhur., Khim.*, 1960, (22), Abstr. No. 88,323.—The method is based on treatment of germanium metal with sulphur vapour at 700° to 800°, which converts the metal into the sulphide and O into SO_2; the SO_2 is then determined colorimetrically with fuchsine - formaldehyde reagent. An apparatus is described. The sensitivity is 2×10^{-4} % of O. K. R. COOK

3644. Methods for the sampling and analysis of tin and tin alloys. Part I. Sampling of ingot tin. British Standards Institution (2 Park Street, London, W.1.). B.S. 3338: Part 1: 1961. 5 pp.—The number of ingots to be sampled in a consignment and the method of sampling are specified.

3645. Methods for the sampling and analysis of tin and tin alloys. Part 2. Tin in ingot tin (aluminium reduction method). British Standards Institution (2 Park Street, London, W.1). B.S. 3338: Part 2: 1961. 9 pp.—Details of the method are given.

3646. Methods for the sampling and analysis of tin and tin alloys. Part 4. Copper in ingot tin and tin - lead solders. British Standards Institution (2 Park Street, London, W.1). B.S. 3338: Part 4: 1961. 6 pp.—A photometric method with HBr - H_3PO_4 is described.

3647. Methods for the sampling and analysis of tin and tin alloys. Part 5. Lead in ingot tin and tin-antimony solders. British Standards Institution (2 Park Street, London, W.1). B.S.3338: Part 5: 1961. 7pp.—A photometric method with dithizone is described.

3648. Methods for the sampling and analysis of tin and tin alloys. Part 6. Copper in high-purity ingot tin. British Standards Institution (2 Park Street, London, W.1). B.S. 3338: Part 6: 1961. 6 pp.—A photometric method with dithio-oxamide is described.

3649. Methods for the sampling and analysis of tin and tin alloys. Part 7. Silver in solders. British Standards Institution (2 Park Street, London, W.1). B.S. 3338: Part 7: 1961. 5 pp.—The volumetric ammonium thiocyanate method of determination is described.

3650. Methods for the sampling and analysis of tin and tin alloys. Part 8. Bismuth. British Standards Institution (2 Park Street, London, W. 1). B.S. 3338: Part 8: 1961. 7 pp.—A photometric method is described for the determination of bismuth in ingot tin, tin - lead solders and white metal bearing alloys.

3651. Methods for the sampling and analysis of tin and tin alloys. Part 11. Tin in solders. British Standards Institution (2 Park Street, London, W.1.) B.S. 3338: Part 11: 1961. 6 pp.—The nickel-coil reduction method for the determination of tin is described.

3652. Methods for the sampling and analysis of tin and tin alloys. Part 12. Sampling of solders. British Standards Institution (2 Park Street, London, W.1). B.S. 3338: Part 12: 1961. 5 pp.—Methods of sampling are described for ingots or bars and for sticks or wire.

3653. Determination of tin with copper aryl- and diaryl-thiosemicarbazides. N. V. Koshkin. *Izv. Výssh. Ucheb. Zavedenií, Khim. i Khim. Tekhnol.*, 1960, **3** (1), 56–58; *Ref. Zhur., Khim.*, 1960, (20), Abstr. No. 80,774.—When Sn^{2+} react with aryl- or diaryl-thiosemicarbazides of Cu^{II}, in acetic acid or aq. ethanolic media, Cu^{2+} are reduced to Cu^{+} and the coloured soln. is decolorised. This is the basis of a titrimetric method for the determination of Sn^{2+} with Cu 1-phenylthiosemicarbazide, although the 1,4-diphenyl-, 1-phenyl-4-*o*-tolyl- or 4-*p*-methoxyphenyl-1-phenyl-thiosemicarbazides may also be used. The reagent is prepared by mixing 25 to 30 ml of 0·04M-1-phenylthiosemicarbazide in acetic acid with 10 to 15 ml of a 0·02M to 0·05M-HNO_3 soln. of $CuSO_4$ or $Cu(NO_3)_2$. The resulting soln. is titrated with the $SnCl_2$ soln. until the blue colour is discharged. Near the end-point the decolorisation takes place quite sharply with 1 or 2 drops of titrant. Towards the end of the titration, the $SnCl_2$ soln. is added slowly with careful stirring. If a turbidity appears, it is removed by adding acetic acid. In determining 4·74 to 28·48 mg of Sn, the max. error was 0·12 mg of Sn; when determining 11·87 to 23·74 mg of Sn in the presence of 5 to 10 mg of Sb, As, P or Zn, the max. deviation was $< 0·17$ mg of Sn. The agreement between the results obtained by this method is better than by the iodimetric procedure. Alkali metals, alkaline-earth metals, Sb, Zn, Pb and As do not interfere. C. D. KOPKIN

3654. Photometric determination of tin in lead. A. G. López. *Quím. e Ind., Bilbao*, 1960, **7** (5), 196–199.—The Sn is pptd. with $Fe(OH)_3$ as carrier, reduced with magnesium and determined with cacotheline. *Procedure*—Prepare a calibration curve by treating aliquots (2 to 7 ml) of standard $SnCl_2$ soln. [1 g of tin dissolved in 300 ml of HCl (1:1) and diluted to 1 litre with H_2O] with 3 ml of conc. HCl and 12 ml of cacotheline soln. (0·25 g in 120 ml of H_2O) and diluting to 25 ml. Read the extinction after 2 to 3 min. in a 1-cm cell against a blank in a Lange photometer with a red filter RG2. Dissolve the sample (containing 3 to 7 mg of Sn) in HNO_3 (1:4) (3·5 ml per g of sample) with gentle heating to expel nitrous fumes. Add 5 ml of 0·8% aq. $Mn(NO_3)_2 \cdot 6H_2O$ soln. and 3 ml of N-$KMnO_4$, boil, and shake. Filter and wash the ppt. with hot H_2O. Repeat the pptn. on the filtrate [2 ml of $Mn(NO_3)_2$ soln. and 3 ml of $KMnO_4$ soln.], filter through the same paper and wash the ppt. with hot H_2O. Then wash the ppt. into the original beaker with hot HCl (2:1) (15 ml), add 2 drops of conc. HNO_3, 1 g of KCl, 2 ml of 1% $FeCl_3$ soln. and a slight excess of aq. NH_3. The pptd. $Fe(OH)_3$ contains all the Sn. Wash the ppt. thrice with cold H_2O, then dissolve it in the minimum amount of hot HCl (2:1). If necessary, reduce the vol. to 10 ml by evaporation at low temp., cool, and add 0·4 g of magnesium metal in small portions, with cooling. Add the soln. to 12 ml of cacotheline soln., make up to 25 ml and measure the extinction as described above. Any ppt. of $PbCl_2$ is removed by centrifuging. Precautions must be taken to avoid oxidation by air, and SO_4^{2-} and NO_3^{-} must be absent. Reducing agents produce a violet colour, but this develops only slowly. Under the conditions described, Ti^{3+}, V^{4+}, Rh^{3+}, Nb^{3+}, As^{3+}, Sb^{3+} and Cr^{3+} do not interfere. S. D. Ross

3655. Determination of lead in copper-base alloys and steel by atomic absorption spectrophotometry. W. T. Elwell and J. A. F. Gidley (Res. Dept., I.C.I. Ltd., Metal Div., Witton, Birmingham, England). *Anal. Chim. Acta*, 1961, **24** (1), 71–78 (in English).—A rapid and accurate method is described. The line Pb 2833·1A was used for absorption measurements and the hollow cathode lamp was operated at 40 mA. The limit of detection is 2 μg of Pb per ml and there is negligible interference from other cations in solution. A. C. R. HARTLEY

3656. Analysis of lead tannate and related chelates by an amperometric method. S. E. Drewes (Paint Industries' Res. Inst., Univ. of Natal, Durban, S. Africa). *Analyst*, 1961, **86**, 104–106.—This method for the determination of Pb was devised for the examination of Pb tannate (a possible pigment for primer paints) and is based on a reversal of the normal amperometric procedure. The chelate is prepared by adding an excess of Pb acetate soln. to an aq. soln. of black-wattle tannin (de-gummed by acetone pptn.). The resulting ppt. is collected and dried *in vacuo*, and 0·2 to 0·3 g is suspended in a mixture of water (20 ml) and ethanol (5 ml). Nitrogen is passed through the soln. for 10 min., the capillary is adjusted to give 3 to 5 drops of mercury per sec., a potential of $-1·2$ or $-1·0$ V *vs.* the S.C.E. is applied, and the soln. is titrated with 0·2N-HNO_3. Results agree well with those by the standard gravimetric procedure. A. O. JONES

3657. Spectroscopic standard samples of titanium and high-temperature alloys. R. E. Michaelis (Nat. Bur. Standards, Washington, D.C.). *Appl. Spectroscopy*, 1961, **15** (1), 7–8.—The N.B.S. has produced three standards of a titanium alloy containing 6 to 11% of Mn and three of an alloy containing 1 to 3% of Cr, 1 to 2% of Fe and 1 to 3% of Mo to add to the already available alloys containing 4 to 7% of Al and 2 to 5% of V. Four standards of complex high-temperature alloys are also announced. All samples are in the form of discs 1·25 in. in diam. and 0·75 in. thick. P. T. BEALE

3658. Determination of titanium in zirconium and zirconium tetrachloride. E. Bowell and P. T. S. Sandon [U.K.A.E.A. (Res. Group), Chem. Div., Chatham Outstation, Riverside, Kent]. Analytical Method AERE–AM 79, 1961. 3 pp.—The reddish-yellow colour given by thymol (**I**) with Ti in conc. H_2SO_4 is used to determine 5 to 100 p.p.m. of Ti with an error $\not> \pm 5\%$. *Procedure*—Dissolve 1 g of metal in dil. HF soln. in a platinum dish or dissolve 2·5 g of the chloride in H_2O (20 ml). Add H_2SO_4 (20 ml) and evaporate to fumes. Cool and transfer the soln. to a 50-ml flask, rinsing the vessel with conc. H_2SO_4. Cool in ice-water and add 10 ml of ice-cold reagent (dissolve 0·5 g of **I** in 5 ml of glacial acetic acid, cool and add dropwise to 95 ml of ice-cold H_2SO_4; this is stable for 2 days). Dilute to 50 ml with ice-cold conc. H_2SO_4, and measure the extinction, with Ilford No. 601 filters and a 4-cm cell. Calibrate by preparing a soln. from pure TiO_2 by fusion with $KHSO_4$. J. W. PRICE

3659. Study of the colour reaction of zirconium with sulphophenylazochromotropic acid. V. M. Peshkova, N. V. Mel'chakova and E. D. Sinitsýna.

Izv. Výssh. Ucheb. Zavedenil, Khim. i Khim. Tekhnol., 1960, **3** (1), 72–74; *Ref. Zhur., Khim.*, 1960, (20), Abstr. No. 80,782.—Conditions are studied for the formation of the complex of Zr^{IV} with 4,5-dihydroxy-3-(*p*-sulphophenylazo)naphthalene-2,7-disulphonic acid (**I**). The reaction is best carried out in 5N-$HClO_4$, with photometry of the resulting soln. at 580 mμ after reducing the pH to between 0·9 and 1·1, with 0·1% aq. **I** soln. as comparison soln. The stability of the complex with time depends on the acidity of the original soln. of Zr^{IV}, the complex being more stable if formed in 9N-$HClO_4$, but after reducing the pH to 1 its light absorption is less than that of the complex obtained in 5N-$HClO_4$. The mol. extinction coeff. at 580 mμ is 18,900; Beer's law is obeyed at concn. of 4 to 40 μg of Zr in 25 ml. The sensitivity of the method is 0·02 μg per ml. The ratio of Zr to **I** in the complex is 1:2. The difference between the results obtained and literature data is due to the different acidities of the soln. in which the complex is formed.

C. D. KOPKIN

3660. **Gravimetric determination of zirconium(IV) with Orange II.** G. Baiulescu and A. Kriza (Lab. de Chim. anorg. şi Anal., Fac. Chim., Univ. "C.I. Parhon," Bucureşti). *Acad. R.P.R., Stud. Cercet. Chim.*, 1960, **8** (3), 541–543.—The acidified soln., containing about 0·2% of Zr, is heated nearly to boiling and an excess of aq. 1% Orange II (C.I. Acid Orange 7) (sodium salt) soln. is added. The ppt. is filtered off, washed with hot water, ignited, and weighed as ZrO_2. If the test soln. is 0·75N in HCl, quant. pptn. may be effected even when the ratio of U to Zr is 220:1. D. R. DUNCAN

3661. **Determination of small amounts of zirconium in ores.** L. I. Kononenko and N. S. Poluéktov. *Trudy Komiss. Anal. Khim., Akad. Nauk SSSR*, 1960, **12**, 132–141; *Ref. Zhur., Khim.*, 1960, (24), Abstr. No. 96,129.—Two photometric methods are developed for the determination of Zr in ores, with arsenazo (**I**) and Alizarin red S (C.I. Mordant Red 3) (**II**). Tervalent Fe is first reduced to Fe^{II} with hydroxyammonium chloride. To remove interference due to Ti, Nb, Mo and Sn when using **I**, and Ta, Ti, Nb and Mo when using **II**, the extinctions of the test soln. with **I** or **II** are measured against the same blank containing EDTA (disodium salt), which selectively masks Zr and does not react with the coloured complexes of the other elements. For the direct determination of Zr in ores (0·1 to 2·0% of ZrO_2), decompose 0·1 g of sample by fusion with a mixture of $Na_2B_4O_7$ and Na_2CO_3, dissolve the melt in water, filter, and wash the pptd. hydroxides; dissolve them in HCl, and determine Zr in an aliquot of the soln. To determine smaller contents of Zr (0·005 to 0·01% of ZrO_2), precipitate Zr as the phenylarsonate in the presence of H_3O_2 from a soln. prepared as described above from a larger sample (0·5 g), filter off the ppt., decompose it on the filter with aq. NH_3, add $AlCl_3$ (3 mg of Al) to the filtrate to precipitate the partially dissolved Zr with the $Al(OH)_3$, and filter through the same filter. Dissolve the ppt. in HCl, extract Zr from the filtrate with oxalic acid soln., destroy oxalic acid with $KMnO_4$ and determine Zr photometrically with **I** or **II**. The completeness of separation of Zr was tested by means of the radioactive isotope ^{181}Hf and found to be 94 to 97%. The results of determining 0·02 to 0·2% of Zr in ores agree well with those of the emission spectrographic method. C. D. KOPKIN

3662. **Anion-exchange studies of zirconium(IV) in citrate solution. Separation from mixtures.** Shripad M. Khopkar and Anil K. De (Jadavpur Univ., Calcutta, India). *Anal. Chim. Acta*, 1961, **24** (2), 134–137 (in English).—The citrate complex of Zr is retained on a column of Dowex 21K anion-exchange resin from a soln. buffered at pH 2·7 to 3·0 with ammonium citrate, and is thus separated from Pb and the fission-product elements Ba, Sr, Cd, Cs and Mo. The Zr is eluted with HCl (0·5N to 2N), the citrate is destroyed with HNO_3 and $HClO_4$, and the Zr is determined as oxide. Antimony, Th, U and V interfere. H. N. S.

3663. **Separation of hafnium from zirconium by anion exchange.** J. L. Hague and L. A. Machlan (Nat. Bur. of Standards, Washington, D.C., U.S.A.). *J. Res. Nat. Bur. Stand., A*, 1961, **65** (1), 75–77.—Hafnium and Zr (≃100 mg of each) can be effectively separated by adsorption as SO_4^{2-} complexes on a strong quaternary amine anion-exchange resin, followed by elution (flow rate 100 ml per hr.) with ≃1 litre of 3·5% H_2SO_4. The initial eluate contains Hf with 10 to 100 p.p.m. of Zr, the next fraction (≃150 ml) contains neither element, and the final eluate contains Zr with 10 to 100 p.p.m. of Hf. The resin bed (7·5 in. high) consists of Dowex 1 (<270 mesh) containing 8% of divinylbenzene cross-linkages. Elution with a mixture of HCl and H_2SO_4 is unsatisfactory. W. J. BAKER

3664. **Spectrographic analysis of hafnium by a point-to-plane technique.** R. C. Brayer, R. F. O'Connell, A. S. Powell and R. H. Gale (Combustion Engng, Inc., Nuclear Div., Mat. Dev. Lab., Windsor, Conn., U.S.A.). *Appl. Spectroscopy*, 1961, **15** (1), 10–13.—An ignited a.c. arc is used for the excitation of solid metallic samples with a graphite counter-electrode. A 3·4-metre Ebert Jarrell-Ash grating spectrograph with 15,000 lines per inch gives sufficient dispersion, and suitable lines are identified in the region 2800 to 3400 A for the determination of Zr (1 to 4%), Al (20 to 150 p.p.m.), Cu (5 to 150 p.p.m.), Fe (20 to 500 p.p.m.), Ti (10 to 100 p.p.m.) and W (20 to 500 p.p.m.), with Hf 2951·9 A as the internal-standard line. Calibration was by means of chemically analysed samples. The reproducibility was satisfactory and comparisons with chemical analyses on buttons melted from hafnium sponge material are reasonable, although discrepancies are shown in the chemical analyses carried out by different laboratories. P. T. BEALE

3665. **Analytical chemistry of thorium—a bibliography.** M. R. Verma, Jitendra Rai and Prabhu Dayal (Nat. Phys. Lab., New Delhi). *J. Sci. Ind. Res., India, A*, 1961, **20** (2), Suppl. 1–24; **20** (3), Suppl. 25–46.—A bibliography of 902 references published from 1940 to 1958 inclusive is presented.

3666. **Detection of thorium with Alizarin red S and its determination with the Weisz ring-oven.** L. Hainberger and S. Cuadrado Sanchez (Inst. de Quím. Pontifícia Univ. Católica, Rio de Janeiro, Brazil). *Mikrochim. Acta*, 1961, (2), 245–249 (in German).—Thorium hydroperoxide forms a purple complex with Alizarin red S (C.I. Mordant Red 3) which can be used for the detection of 0·05 μg of Th in neutral soln. The reagent is 0·1% aq. Alizarin red S soln. containing 10% of NH_4NO_3 and 15% of H_2O_2. The reaction is not specific, and samples containing other metals, *e.g.*, minerals, must be subjected to a separation procedure in which the sample is fused with solid NaOH, acidified

with HNO_3, and made alkaline with aq. NH_3. Thorium is pptd. as the fluoride with excess of NaF and converted into the hydroxide with aq. NH_3; this is dissolved in HNO_3 containing $Al(NO_3)_3$ and extracted into tri-n-butyl phosphate in xylene. Finally the Th is re-extracted into water and subjected to the spot test or determined quantitatively with the ring-oven. W. T. CARTER

3667. **Spectrophotometric determination of traces of boron in thorium.** Hiroshi Onishi, Nasumi Ishiwatari and Hitoshi Nagai (Japan Atomic Energy Res. Inst., Tokai, Ibaraki-ken). *Bull. Chem. Soc. Japan*, 1960, **33** (12), 1686–1688.—The sample (thorium oxide or metal) is dissolved in conc. H_3PO_4, the soln. is diluted with water, the B is separated by distillation as trimethyl borate, and determined by the curcumin method (*Ibid.*, 1960, **33**, 830). The error is $\pm 0{\cdot}1$ p.p.m. for 0·2 to 1·0 p.p.m. of B. I. JONES

3668. **Recovery of radioactive thorium indicator on an ion-exchange resin.** A. M. Petrov, I. A. Korshunov and V. A. Sidorov. *Trudy Khim. i Khim. Tekhnol.*, 1959, (3), 498–499; *Ref. Zhur., Khim.*, 1961, (3), Abstr. No. 3D81.—The isotope ^{234}Th is separated from U-containing soln. by addition of hydroxylamine, to give the anionic complex of U, and passage through the cation-exchange resin KU-1. The small amount of adsorbed U is eluted with 0·5N-HCl, and the ^{234}Th is then eluted with 4N-HCl. K. R. COOK

3669. **Determination of hydrazoic acid and ferric ion by spectrophotometric measurement of the ferric azide complex.** E. K. Dukes and R. M. Wallace (Savannah River Lab., E. I. du Pont de Nemours & Co., Inc., Aiken, S.C., U.S.A.). *Anal. Chem.*, 1961, **33** (2), 242–244.—The three procedures given permit the determination, either separately or simultaneously, of HN_3 and Fe^{3+} in soln. of HNO_3 containing hydrazine, Fe^{3+}, Fe^{2+} and HN_3. (*i*)—If either HN_3 or Fe^{3+} are present, a known vol. of 0·5M-$Fe(NO_3)_3$ or NaN_3, respectively, is added to the sample soln. and, after diluting the mixture, the concn. of HNO_3 is determined by titration with NaOH soln. (any Fe^{3+} must be complexed with oxalate). The extinction of the ferric azide complex is then measured at 460 mμ and 23° against a reagent blank. (*ii*)—If Fe^{3+} and HN_3 are both present, but in concn. insufficient to give a measurable extinction, the same procedure can be used, but the concn. of the added component must be very high or the acidity must be reduced. (*iii*)—If Fe^{3+} and HN_3 are both present in sufficient concn. to produce a measurable extinction, an aliquot of the sample soln. is diluted with 0·5M-HNO_3 and the extinction of the ferric azide complex is measured. A known concn. of either Fe^{3+} or HN_3 is then added to another aliquot similarly diluted, and the increased extinction is measured. In all three procedures the concn. of Fe^{3+} and HN_3 are calculated from equations, taking into account the concn. of HNO_3. The standard deviation is 0·0016 (10 analyses for molarities from 0·0075 to 0·305); max. sensitivity is attained at low concn. of HNO_3. Max. concn. of 0·25M-Fe^{3+} and 0·12M-HN_3 were used. W. J. BAKER

3670. **The absorption spectrum of nitrous acid in tributyl phosphate, and its application to analyses for nitrous acid.** J. Woodhead (Chem. Div., A.E.R.E. Harwell, England). A.E.R.E. Report R 3432, 1960. 10 pp.—Concn. of NO_2^- as low as 5×10^{-4}M can be determined accurately by stirring an aliquot of the aq. soln. for 5 min. with a known vol. of 20 to 100% (v/v) tributyl phosphate soln. in kerosine (previously equilibrated with 0·25M-$HClO_4$), adjusting the acidity to $<0{\cdot}5$M with either H_2O or $HClO_4$. The mixture is centrifuged, the spectrum of the organic phase is recorded between 320 and 400 mμ and the concn. of NO_2^- is then calculated from the molar extinction coeff. for the peaks at 375·5 and 390·5 mμ. When other extractable species are present the organic phase must be washed three times with twice its vol. of H_2O before recording the spectrum. Beer's law is followed over the range 0·0005 to 0·01M-NO_2^-.

3671. **Rapid method for the determination of ammonia (combined) and phosphate in the system of diammonium phosphate and dipotassium phosphate.** B. Paschkes and B. Bernas (Israel Mining Industries Lab., Haifa, Israel). *Anal. Chim. Acta*, 1961, **24** (1), 5–10 (in English).—*Procedure*—The PO_4^{3-} ($\simeq$60 mg) are determined in one 50-ml aliquot of sample soln. by direct titration with 0·1N-HCl, with methyl orange as indicator. Excess of 0·1N-NaOH is added to a second aliquot of sample soln., and NH_3 ($\simeq$15 mg) is removed by boiling. Titration of the cooled soln. with 0·1N-HCl, with methyl orange as indicator, gives the sum of PO_4^{3-} and unchanged NaOH. The content of NH_3 may be deduced from the difference between the two titrations. A. C. R. HARTLEY

3672. **Separation of phosphate ion from arsenate ion by solvent extraction.** H. H. Ross and R. B. Hahn (Dept. of Chem., Wayne State Univ., Detroit, Mich., U.S.A.). *Talanta*, 1961, **7** (3–4), 276–280 (in English).—Various solvents and solvent mixtures were studied as selective extractants for PO_4^{3-} from soln. containing AsO_4^{3-}. Butanol - $CHCl_3$ was the most promising system; the amounts of PO_4^{3-} and AsO_4^{3-} extracted by a 4:1 mixture were 94·97 and 4·7%, respectively. Addition of PO_4^{3-} did not significantly reduce the extraction of AsO_4^{3-} at this solvent ratio. P. D. PARR-RICHARD

3673. **The evolution of arsine from alkaline solution.** A. J. Hegedüs and M. Dvorszky (Forschungsinst. für die Nachrichtentech. Ind., Tungsram, Budapest, Hungary). *Mikrochim. Acta*, 1961, (2), 186–190 (in German).—The amount of AsH_3 evolved from alkaline soln. depends on the alkalinity of the soln. and the purity, activity, and dimensions and nature of the surface of the aluminium used for the reduction. Recoveries of 95 to 100% are obtained for 100 μg of As with 0·5N-KOH and aluminium filings (99·99% purity) activated immediately before use by immersion in 0·1N-KOH containing 0·5 p.p.m. of As. Quinquevalent As is not reduced under the conditions of the test, and a prior reduction in acid soln. is necessary. In soln. containing W, this causes the pptn. of tungstic acid, which adsorbs the As. W. T. CARTER

3674. **Sources of error in the volumetric microdetermination of arsenic by the method of Bodnár, Szép and Cieleszky.** A. J. Hegedüs and M. Dvorszky (Forschungsinst. für die Nachrichtentech. Ind., Tungsram, Budapest, Hungary). *Mikrochim. Acta*, 1961, (2), 181–185 (in German).—Low results in this method (*cf. Z. anal. Chem.*, 1939, **115**, 412) are caused by the presence of cyanate in the KCN used in the titration, impurities in the tin used for the generation of AsH_3, the formation of As_2O_3 in the heated silica tube, the presence of traces of

oxidising agents in the reagents and the existence of unfavourable equilibria in some of the reactions.
W. T. CARTER

3675. **Volumetric micro-determination of traces of arsenic in tungsten, molybdenum and other metals.** A. J. Hegedüs and M. Dvorszky (Forschungsinst. fur die Nachrichtentech. Ind., Tungsram, Budapest, Hungary). *Mikrochim. Acta*, 1961, (2), 169–180 (in German).—The modified Marsh test of Bodnár *et al.* (*Z. anal. Chem.*, 1939, **115**, 412) is applied to the determination of traces of As in tungsten and tungstic oxide. Tungstic oxide is analysed directly after being dissolved in alkali. Metallic tungsten is converted into WO_3 by slow oxidation at 600° or by dissolution in HNO_3, H_3PO_4, or HNO_3 - H_3PO_4 - H_2O_2. By using an empirical factor obtained by calibration with soln. of known As content, an accuracy of ±2·3% can be achieved for ≃70 μg of As in 1 g of tungsten. The method can also be used for the determination of As in metallic molybdenum, zinc, sodium, copper, lead, magnesium, barium, manganese, iron, aluminium, calcium and mercury. W. T. CARTER

3676. **Polarographic analysis using potassium iodide as supporting electrolyte. III. Polarographic behaviour of tervalent arsenic.** Teiichi Matsumae and Ryozo Nakashima (Govt. Ind. Res. Inst., Nagoya, Japan). *Anal. Chim. Acta*, 1961, **24** (2), 192–199 (in English).—Tervalent As yields two polarographic waves in 0·1M-KCl. The effects of the height of the mercury column, temp. and pH are investigated. The sum of the wave heights bears a linear relationship to the concn. of As^{3+} at concn. < 0·004M and at pH 1·9 to 2·5. Dodecyltrimethylammonium chloride (0·001%) is used as max. suppressor. H. N. S.

3677. **Photometric determination of antimony with methylfluorone.** S. Meyer and O. G. Koch (Chem. Lab., Neunkircher Eisenwerk A.-G., Neunkirchen, Saar). *Z. anal. Chem.*, 1961, **179** (3), 175–186 (in German).—To prepare the reagent, dissolve methylfluorone (2,6,7-trihydroxy-9-methylfluorone) (0·05 g) in 2N-NaOH (5 ml), add water (25 to 30 ml), ethanol (50 ml) and, with cooling, conc. HCl (1·6 ml) and dilute to 100 ml with water. *Procedure*—To the test soln. (≃N in HCl and containing 5 to 100 μg of Sb) add Clark and Lubs buffer soln. (pH 2) (5 ml), 1% poly(vinyl alcohol) soln. (1 ml) and reagent (1 ml). Dilute to ≃40 ml, adjust the pH to 2·0 with 2N-NaOH or 2N-HCl, dilute to 50 ml with water and measure the extinction at 495 mμ against water. Subtract the extinction of a reagent blank. Beer's law is obeyed over the range 0·2 to 4·0 μg of Sb per ml. Determinations of 1 μg of Sb per ml gave a standard deviation of ± 0·018. The reaction of 53 other cations with the reagent and the influence of 25 anions on the reaction are recorded.
A. J. BENNETT

3678. **New colour reaction for the detection of stibine.** G. Ciuhandu and M. Rocsin (Inst. de Igienă, Lab. de Toxicol., Timişoara, Romania). *Acad. R.P.R., Stud. Cercet. Chim.*, 1960, **8** (3), 537–539.—Stibine in the gas obtained by reducing with nascent H a soln. containing as little as 1 g of Sb in 5 ml may be detected by the greyish-yellow to brown colour produced on passing the gas through 5 ml of an alkaline soln. of Ag *p*-sulphamoylbenzoate, prepared by mixing 1 vol. of 0·1M-Na-*p*-sulphamoylbenzoate with 1 vol. of 0·1M-$AgNO_3$ and adding 0·5 vol. of M-NaOH. D. R. DUNCAN

3679. **Separations involving sulphides. I. Separation of quinquevalent antimony from alkaline earths.** G. B. S. Salaria (Chem. Dept., Govt. Coll., Dharmsala, India). *Z. anal. Chem.*, 1961, **179** (2), 91–92 (in English).—The method previously described (*Anal. Abstr.*, 1959, **6**, 2459) has been extended to include antimony. T. R. ANDREW

3680. **Liquid - liquid extraction of vanadium(V) with tributyl phosphate.** Santosh K. Majumdar and Anil K. De (Jadavpur Univ., Calcutta, India). *Anal. Chem.*, 1961, **33** (2), 297–299.—Approx. 25 mg of V^V can be extracted (98 to 99% recovery) as $VOCl_3.2$(solvent) from 5N to 6N-HCl with 100% tributyl phosphate in ≃5 min. After back-extraction into H_2O, the V can be determined volumetrically. None of the following ions interferes—Cu^{2+}, Hg^{2+}, Co^{2+}, Ni^{2+}, Ba^{2+}, Bi^{3+}, Fe^{3+}, Cr^{3+}, Th^{4+}, U^{6+}, Mo^{6+}, PO_4^{3-} and $EDTA^{4-}$, although Cu^{2+}, Co^{2+}, U^{6+}, Fe^{3+}, Th^{4+} and Mo^{6+} are co-extracted with the V. Citrate and tartrate must be absent.
W. J. BAKER

3681. **Study of the co-precipitation of vanadyl ions with aluminium hydroxide.** V. L. Zolotavin and Yu. I. Sannikov. *Trudy Ural'sk. Politekh. Inst.*, 1959, (8), 228–233; *Ref. Zhur., Khim.*, 1960, (20), Abstr. No. 80,700.—The pH values at which $Al(OH)_3$ and $VO(OH)_3$ begin to precipitate from pure soln. and when both are present are determined. Complete co-pptn. of VO^{2+} with $Al(OH)_3$ occurs when the relative content of V is ⩾15%. It is suggested that the main process in the co-pptn. is the formation of a solid solution. The VO^{2+} are strongly held in the ppt., are not converted into hypovanadate and are not oxidised. The co-pptn. method enables the sensitivity of qual. reactions for V to be increased. C. D. KOPKIN

3682. **Determination of small amounts of vanadium in ores.** E. Pavlíková (Inst. Res. Ores, Prague). *Sb. Prac. Úst. Pro Výzk. Rud III*, 1958–59, 242–248.—A photometric tungstovanadophosphate method is described. Iron, Ni, Co, Mn, Cr, Sn, Bi, Sb and Mo are removed by mercury electrolysis, and any residual Ti is masked with NaF. The method is suitable for samples containing 0·001% of V. *Procedure*—Heat the finely powdered sample (0·5 to 3 g) with a mixture of equal vol. of HNO_3 (1:1) and H_2SO_4 (1:1) (20 to 25 ml). Evaporate to dryness, add H_2O, heat, filter and wash. If necessary, remove SiO_2 by the usual method. Evaporate the filtrate to ≃80 ml and electrolyse for 1 hr. Then oxidise V^{IV} with bromine water, heat and transfer to a 50-ml flask and make up to vol. To an aliquot in a 25-ml flask add HCl (1:1) (0·5 ml), H_3PO_4 (1:2) (5 ml) and 0·25M-Na_2WO_4 (1 ml). Dilute with H_2O to vol., mix, and after 15 min. measure the extinction with violet filter S42. J. ZÝKA

3683. **Gravimetric determination of niobium as 8-hydroxyquinolinate.** A. A. Mambetov and N. A. Pzaeva. *Azerbaidzh. Sel.-Khoz. Inst.*, 1960, **11**, 221–227; *Ref. Zhur., Khim.*, 1960, (22), Abstr. No. 88,299.—*Procedure*—Fuse the sample with a 40-fold amount of $K_2S_2O_7$ in a quartz dish at 700° to 800° and leach with 20% tartaric acid soln. (40 to 50 ml). Dilute the soln. so as to obtain a tartaric acid content of 1 to 2 g and an Nb_2O_5 concn. of 20 to 50 mg in 100 to 120 ml, neutralise with aq. NH_3 to a pH of 4 to 7, heat to 70° to 80°, precipitate with a 2 to 3-fold excess of 3% ethanolic 8-hydroxyquinoline soln. and boil for 30 min. Allow the

ppt. to settle (15 to 20 min.), collect it in a sintered glass crucible (No. 4), wash it free from 8-hydroxyquinoline with warm H_2O and dry it at 110° to 115°.
K. R. Cook

3684. **Quantitative spectrographic determination of niobium in carbonaceous samples with pneumatic introduction of powders into the arc discharge.** R. S. Rubinovich. *Inform. Byull. Inst. Geol. Arktiki*, 1959, (16), 61–68; *Ref. Zhur., Khim.*, 1960, (21), Abstr. No. 84,454.—The substance is blown directly upwards from a special vessel into the arc gap between two horizontal carbon electrodes [*Ref. Zhur., Fiz.*, 1960, (7), Abstr. No. 18,613]; 3 to 4 mg of sample are blown into the discharge (current strength 16 to 18 amp.) in 15 sec. Samples and standards are first mixed with an equal amount of carbon powder to which Mo is added. The values of ΔS for the lines Nb 2950·9 and Mo 2934·3 A change during the blowing process, because of fractionation of particles according to their size, thus producing large errors. For smooth delivery of particles of various sizes, the samples and standards are treated with HF (to 0·2 g of sample add 20 mg of acid and evaporate at 200° for 1 hr.). Calibration curves constructed from standards on various bases do not coincide but, by allowing for the background, the graphs can be made to agree to within ± 10%. The results for a large number of determinations agree well with those by chemical analysis. The error is ≃ ± 7%.
C. D. Kopkin

3685. **Precipitation and determination of tantalum and niobium from homogeneous solution with 3,3′,4′,5,7-pentahydroxyflavanone.** F. L. Chan (Aeronaut. Res. Lab., Wright-Patterson Air Force Base, Ohio, U.S.A.). *Talanta*, 1961, **7** (3–4), 253–263 (in English).—On heating 3,3′,4′,5,7-pentahydroxyflavanone (**I**) in 6 to 9N acid soln., the corresponding flavone, which quant. precipitates Ta and Nb, is slowly generated. *Procedure for Ta or Nb*—Fuse the sample (> 20 mg of the oxide of Ta or Nb) with 1 g of $KHSO_4$, cool and extract the melt with hot conc. H_2SO_4 (5 × 5 ml). Cool the extract and pour it into 30 ml of satd. ammonium oxalate soln. to give a clear soln. Add a hot soln. of **I** (0·5 to 1·5 g of **I** in 45 ml of H_2O) and boil for 1 hr. (15 hr. for Nb). Add H_2O (50 ml) and set aside for 1 hr.; filter, and wash the ppt., first with 1% **I** soln. in N-H_2SO_4 (4 × 5 ml) and then with satd. aq. **I** soln. (6 × 5 ml). Ignite the paper and ppt. in platinum to const. wt. The separation of Ta and Nb is also described. Titanium should be absent.
P. D. Parr-Richard

3686. **Determination of mixed tantalum and niobium pentoxides.** Sh. G. Melamed, A. K. Rusanov and M. G. Zemskova. *Trudy Komiss. Anal. Khim., Akad. Nauk SSSR*, 1960, **12**, 65–70; *Ref. Zhur., Khim.*, 1961, (3), Abstr. No. 3D84.—For mixtures of the pentoxides containing 5 to 99% of Ta_2O_5, a spectrographic pressed-pellet technique, with a multisource discharge, is used. For Ta_2O_5 contents of <5% or Nb_2O_5 contents of <1%, a 10-amp. d.c. discharge is used. Titanium (>3%) interferes, but may be corrected for. Full analytical details are given, including precisions attained and details of the preparation of standards.
K. R. Cook

3687. **Use of phenylarsonic acid in turbidimetry. Determination of tantalum.** R. Saint-James and T. Lecomte (Centre d'Études Nucléaires de Saclay, Dépt. de Métall., Service A.R.C.A., Gif-sur-Yvette, Seine et Oise, France). *Anal. Chim. Acta*, 1961, **24** (2), 155–160 (in French).—The Ta content (0·2 to 2%) of uranium - tantalum alloys is determined with a relative error of < ± 0·5%. The turbidity developed on adding phenylarsonic acid soln. to a soln. of the sample in 2N to 3N-H_2SO_4 is stabilised by the addition of glycerol, and the extinction is determined at 350 mμ, with the application of appropriate blank corrections. An equiv. atomic concn. of Nb is tolerated if H_2O_2 is present. Zirconium interferes at an atomic ratio of Zr to Ta of > 5:1. Iron, if present, is reduced with ascorbic acid.
H. N. S.

3688. **Volumetric determination of sulphate ion.** B. A. Ryazanov. *Nauch. Trudy Mosk. Tekhnol. Inst. Legkoĭ Prom.*, 1960, (16), 62–65; *Ref. Zhur., Khim.*, 1960, (24), Abstr. No. 96,153.—A method is proposed for the direct titration of SO_4^{2-} in soln. of $Cr_2(SO_4)_3$ or $Al_2(SO_4)_3$ with $Pb(NO_3)_2$ soln., with dithizone as indicator. To a known vol. (10 to 20 ml) of soln. add 3 ml of ≃0·1N-HCl, 15 ml of acetone and 10 drops of a satd. soln. of dithizone in 100% acetone, and titrate slowly, with continuous stirring, with ≃0·1N-$Pb(NO_3)_2$ till the dithizone colour changes from green to red. Towards the end of the titration, add the $Pb(NO_3)_2$ soln. dropwise, shaking and allowing the soln. to stand for ≃1 min. The titration must be carried out in daylight. Titrating to a pink ppt. gives a result low by 4·32%, and to a bright-red ppt. a result high by 1·9%. With 29 to 76 mg of SO_4^{2-} the error was 0·63 to 0·99%.
C. D. Kopkin

3689. **Indirect determination of sulphate by non-aqueous titrimetry.** G. Goldstein, O. Menis and D. L. Manning (Anal. Chem. Div., Oak Ridge Nat. Lab., Tenn., U.S.A.). *Anal. Chem.*, 1961, **33** (2), 266–268.—From 1 to 6 mg of SO_4^{2-} in an aliquot of the aq. soln. can be determined, in the presence of such normally interfering ions as UO_2^{2+} and Fe^{3+}, by pptn. with an excess of 0·05N-Ba acetate, the excess of which is determined by potentiometric titration with 0·03N-$HClO_4$ in glacial acetic acid. The H_2O is eliminated by the addition of acetic anhydride (6 ml per ml of soln.) and boiling the mixture for ≃2 min.; addition of ≃10 ml of glacial acetic acid at the same time prevents pptn. of inorg. salts other than $BaSO_4$. Co-pptn. effects and minor cationic or anionic interferences are discussed. The precision is within 1% and the accuracy is equiv. to that for the cation exchange - $BaCl_2$ method. The procedure is suitable for the determination of total SO_4^{2-} in soln. of reactor fuels.
W. J. Baker

3690. **Determination of small amounts of selenium in anodic copper.** A. I. Zelyanskaya and L. S. Gorshkova. *Trudy Inst. Metallurg. Ural'sk. Fil. Akad. Nauk SSSR*, 1960, (5), 137–139; *Ref. Zhur., Khim.*, 1960, (24), Abstr. No. 96,154.—The method is based on the removal of Se from Cu by cation exchange, with subsequent determination of Se by iodimetric titration. Dissolve 2 g of the anodic copper in HNO_3 (1:1), evaporate the soln. with H_2SO_4, and add 225 ml of water (to dissolve the salts), 0·1 to 0·2 g of citric acid crystals (to complex Fe) and 25 ml of conc. aq. NH_3. Pass the resulting soln. at a rate of 6 to 8 ml per min. through a column (60 cm × 2·5 cm in diam.) packed with a 45-cm layer of Wofatit R (NH_4^+ form), which retains only the cuprammonium complex. Wash the column with aq. NH_3 (1:9), evaporate the percolate and wash soln. to 150 to 200 ml, neutralise

with HCl to Congo red, add excess of HCl (15 ml), a known vol. of standard $Na_2S_2O_3$ soln. and 2 to 3 ml of 1% starch soln., and titrate the unchanged $Na_2S_2O_3$ with iodine. The method has been used successfully to determine 0·011 to 0·039% of Se in industrial samples of anodic copper.

C. D. KOPKIN

3691. **Determination of selenium in sludge containing platinum.** V. I. Murashova. *Trudy Ural'sk. Politekh. Inst.*, 1960, **94**, 161–167; *Ref. Zhur., Khim.*, 1960, (22), Abstr. No. 88,332.—Treat the sludge (0·5 g) by heating with conc. HNO_3 (25 to 30 ml), add Na_2CO_3 until the first appearance of a hydroxide ppt., and then 20% NaOH soln. (20 ml), and hydroxyammonium chloride (**I**) (4 g). Boil for 2 to 3 min., cool, dilute to 100 ml and filter off the residue (Pt and Pd) with a dry filter. Neutralise the filtrate (50 ml) to litmus, add conc. HCl (5 mg per 100 ml of soln.) and urea (2 g), boil for 1 to 2 min., add **I** (5 g) and boil for another 15 min. Filter off the residue (Se), wash it with hot HCl (1:20), dissolve the ppt. by heating in conc. HCl (10 ml) plus conc. HNO_3 (6 drops), dilute, add urea and determine Se^{4+} iodimetrically. The error is 2%.

K. R. COOK

3692. **Indirect potentiometric method for the micro-determination of selenium.** H. Hahn and H. Bartels (Chem. Inst., Univ. Würzburg, Germany). *Mikrochim. Acta*, 1961, (2), 250–261 (in German).—The method of Hahn and Viohl (*cf. Anal. Abstr.*, 1956, **3**, 2069) is adapted to the determination of micro amounts of Se by using the procedure for the potentiometric titration of micro amounts of Ag^+ developed by Shiner and Smith (*Anal. Abstr.*, 1956, **3**, 3037). To obtain accurate results it is necessary to destroy excess of hydrazine by heating at 105° for 15 min. before the titration. Since very dilute soln. of $AgNO_3$ are photo-sensitive, it is essential to work in red light. The accuracy ranges from $\simeq \pm 2\%$ for 1 μg of Se to $\pm 1\%$ for 100 μg of Se. A twofold excess of Te does not interfere.

W. T. CARTER

3693. **Spot detection and quantitative determination of selenium and tellurium.** I. M. Korenman, V. G. Ganina and N. V. Kurina. *Trudy Khim. i Khim. Tekhnol.*, 1959, (2), 369–375; *Ref. Zhur., Khim.*, 1960, (23), Abstr. No. 92,080.—The reduction of selenites and tellurites is used for the detection and determination of elementary Se and Te. The best reducing agents are thiourea and hydroxyammonium chloride for selenites, and $SnCl_2$ for tellurites. When Na_2SeO_3 is treated with thiourea in the cold or with hydroxyammonium chloride with heating, a red ppt. or pink colour is formed, depending on the Se content. The detectable minimum of Se is 5 μg per ml at a limiting concn. of 1 in 2×10^5. The sensitivity of the reaction is increased five times by flotation of the elementary Se with ether, which is more suitable for this purpose than $CHCl_3$ or dichloroethane. Interference in the detection of Se is caused by Au, Pt and Pd, which are also reduced to metals in acid and alkaline media. No interference is caused by Co, Al, Bi, Ni, Pb, Cu or Ag. When K_2TeO_3 is treated with 10% $SnCl_2$ soln. in the cold, a black ppt. or brown colour is formed, depending on the Te content. The detectable minimum for Te is 10 μg per ml at a limiting concn. of 1 in 10^4. No interference in the detection of Te is caused by 100-fold amounts of Fe, Al, Bi, Co, Cu, Ni, Mg, Ba, Pb or Ag. The interference of H_2SeO_3 is removed by the action of thiourea, which reduces H_2SeO_3 to Se, leaving unchanged H_2TeO_3 in soln. Gold is pptd. with NaOH soln. in the presence of hydroxyammonium chloride. Procedures are given for determining Se with thiourea in the presence of other ions. The standard-series method can be used to determine 20 to 100 μg of Se per ml, and the nephelometric method for 2·5 to 25 μg of Se per ml, with mean errors of 5% and 1%, respectively. Tellurium can be determined with $SnCl_2$ in the presence of other ions by the nephelometric and standard-series methods with mean errors as low as 2·5%.

C. D. KOPKIN

3694. **Determination of selenium and tellurium in bronze and copper.** V. I. Murashova and L. P. Bol'shakova. *Trudy Ural'sk. Politekh. Inst.*, 1960, (94), 158–160; *Ref. Zhur., Khim.*, 1960, (21), Abstr. No. 84,489.—Titrimetric methods are proposed for the determination of small amounts (0·048 to 0·098%) of Se and Te in bronze and copper. *Procedure for Se*—Dissolve 1 g of sample by heating with conc. HNO_3, add 1 g of $Pb(NO_3)_2$, and treat with an excess of aq. NH_3; Cu dissolves and Se and Te co-precipitate with $Pb(OH)_2$. Filter off the ppt., wash it with hot water, and dissolve it on the filter with a hot mixture of HCl and NaCl [1 litre of satd. NaCl soln. and 300 ml of HCl (1:1)]. Heat the soln. to dissolve the $PbCl_2$ and precipitate Se by heating for 15 min. with a 10% $SnCl_2$ soln. Filter off the ppt., wash it with hot HCl (1:20), transfer the filter to the pptn. flask, treat with 10 ml of conc. HCl and 5 or 6 drops of HNO_3, dilute to 150 ml, add 5 g of urea and boil. To the cooled soln. add excess of 0·03N-$Na_2S_2O_3$ and back-titrate with iodine soln., with starch as indicator. *Procedure for Te*—Carry out the preliminary procedure as described above, then to the soln. to be titrated add 10 ml of 30% KI soln. and titrate the resulting complex with 0·03N-$Na_2S_2O_3$. The error of the determinations is 0·03% (abs.) for Se and 0·001% (abs.) for Te.

C. D. KOPKIN

3695. **Spectrographic analysis of tellurium.** V. V. Polyakova and V. V. Fedorova. *Spektr. Anal. v Tsvet. Metall. M., Metallurgizdat*, 1960, 172–175; *Ref. Zhur., Khim.*, 1961, (3), Abstr. No. 3D153.—Silver, Cu, Bi, Sb, Pb, Mg, As, Au, Si, Al and Fe in the range 10^{-4} to 10^{-2}% are determined by an a.c. arc technique with a mean error of 10 to 20%.

K. R. COOK

3696. **Influence of iron on the colorimetric determination of chromium.** R. K. Korabel'nik. *Izv. Vyssh. Ucheb. Zavedenii, Khim. i Khim. Tekhnol.*, 1960, **3** (1), 189–192; *Ref. Zhur., Khim.*, 1960, (20), Abstr. No. 80,789.—The influence of Fe^{3+} on the photometric determination of Cr with diphenylcarbazide (**I**) is studied. The presence of large amounts of Fe^{3+} destroys the linearity of the calibration curve; H_3PO_4 slightly reduces the influence of Fe^{3+}, but decreases the intensity of the colour and increases the dispersion of the points on the curve. Potentiometric titration with $(NH_4)_2SO_4.FeSO_4.6H_2O$ soln. of a mixture of $Cr_2O_7^{2-}$ and Fe^{3+} has shown that Fe^{3+} cause an intermediate break in the potential curve, a shift of the end-point, and a decrease in the potential jump at the end-point. In the presence of H_3PO_4 the potentiometric titration curve is slightly more regular, but the end-point is still displaced. On titrating a mixture of $Cr_2O_7^{2-}$ and H_3PO_4 with $(NH_4)_2SO_4.FeSO_4.6H_2O$ soln. the end-point is displaced and the potential jump is decreased. The experiments are poorly reproducible and depend on the temp., which

explains the slow (≃50 min.) establishment of the equilibrium potential. Light has a strong influence on the reaction between $Cr_2O_7^{2-}$ and $(NH_4)_2SO_4$.$FeSO_4$.$6H_2O$, which takes place only in bright light. The reduced reproducibility of the determination of Cr in the presence of Fe^{3+} and H_3PO_4 is due to a change in the rate of oxidation of **I** by $Cr_2O_7^{2-}$, and to the reaction of **I** with the Fe^{3+} - H_3PO_4 complex (increasing the extinction).

C. D. KOPKIN

3697. **Spectrophotometric determination of chromium in uranium with 8-hydroxyquinaldine.** Kenji Motojima and Hiroshi Hashitani (Atomic Energy Res. Inst., Ibaraki-ken, Japan). *Anal. Chem.*, 1961, **33** (2), 239–242.—From 3 to 100 μg of Cr^{3+} in 50 ml of an acid soln. of the sample can be determined by extraction, with $CHCl_3$ at pH 5·3 to 6, of the Cr - 8-hydroxyquinaldine complex (after heating this at 60° to 70° for ≃ 8 min. and then cooling), and measuring the extinctions of the extract at 410 mμ and 580 mμ against a blank as reference (*cf. Japan Analyst*, 1960, **9**, 151). Uranium (≯ 2·5 g is permissible) must be selectively masked with acetic acid, whilst Fe, Cu, Ni, Mo, V and Ti must be removed by washing the extract with a soln. containing 2M-ammonium carbonate, M-KCN and M-hydroxyammonium sulphate. The extinction at 580 mμ provides for a correction to be made for the small amount of residual Fe complex. Relatively high concn. of Cl^-, NO_3^- and SO_4^{2-} do not interfere. The standard deviation is 1·1% (several analyses), and the lower limit of determination is 1 p.p.m. of Cr.

W. J. BAKER

3698. **Gravimetric determination of molybdenum and its separation from other metals with *N*-benzoyl-*N*-phenylhydroxylamine.** S. K. Sinha and S. C. Shome (Presidency College, Calcutta, India). *Anal. Chim. Acta*, 1961, **24** (1), 33–36 (in English).—Sexavalent Mo is pptd. at 60° from an acid soln. by ethanolic *N*-benzoyl-*N*-phenylhydroxylamine. The ppt. may be weighed directly or ignited at 500° to 525° and weighed as MoO_3. In either case the accuracy is ≃ ±0·5%. The determination may be carried out in the presence of Cr^{VI}, Co^{II}, Ni^{II}, Cu^{II}, Fe^{III} and V^{V}.

A. C. R. HARTLEY

3699. **Colorimetric determination of molybdenum by the visual method with Acid Chrome blue 2K as reagent.** V. P. Kondratova and V. I. Petrashen'. *Trudy Novocherk. Politekh. Inst.*, 1959, **97**, 155–162; *Ref. Zhur., Khim.*, 1960, (20), Abstr. No. 80,794.—In the presence of Mo^{VI} the crimson colour of Acid Chrome blue 2K (C.I. Mordant Green 28) (**I**) is changed to bluish-violet (max. absorption at 619 mμ). At pH 2·2 and with a content of **I** of 0·2%, Beer's law is obeyed for concn. of 2 to 9 μg of Mo per ml. The colour develops in 10 to 15 min. and is independent of temp. and order of introducing the reagents. On the basis of the results obtained, a colorimetric standard-series method has been developed. With concn. of 2 to 12·5 μg of Mo per ml, the error of the determination is 0·8 to 17%. No interference is caused by the following (the limiting ratios are given in parentheses)—Cl^- (1420), NO_3^- (1942), SO_4^{2-} (1000), PO_4^{3-} (633), SiO_3^{2-} (150), K^+ (1560), Na^+ (500), Al^{3+} (40), Fe^{3+} (5), Fe^{2+} (20), Mn^{2+} (250), Ni^{2+} (500), Cr^{3+} (75), W^{6+} (40) and Ti^{4+} (400).

C. D. KOPKIN

3700. **Radiochemical determination of molybdenum by solvent extraction.** W. J. Maeck, M. E. Kussy and J. E. Rein (Atomic Energy Div., Phillips Petroleum Co., Idaho Falls, U.S.A.). *Anal. Chem.*, 1961, **33** (2), 237–238.—The determination of ^{99}Mo (half-life 6·55 ± 0·22 hr.) in mixtures of young fission-products is based on a double extraction of the benzoin α-oxime complex into ethyl acetate, with subsequent stripping into N-HCl and pptn. of $PbMoO_4$. The ppt. is collected on a fine filter-disc, mounted on an aluminium plate, and a β-count is made with a gas-flow proportional counter. Treatment of the sample before extraction consists in adding (*i*) $KMnO_4$ and molybdenum carrier to ensure chemical identity, (*ii*) a hold-back carrier (KI) to decrease the extraction of iodine, and (*iii*) Fe^{III} as scavenger. The procedure, which avoids the lengthy wet-oxidation with $HClO_4$ and ensures excellent decontamination, is modified slightly for water samples low in Mo. The standard deviation is ≃2·4% and an analysis takes ≃75 min.

W. J. BAKER

3701. **Spectrographic determination of cadmium, antimony, bismuth, lead and tin in tungsten and molybdenum.** É. E. Vainshtein, Yu. I. Belyaev and M. V. Akhmanova. *Trudy Komiss. Anal. Khim., Akad. Nauk SSSR*, 1960, **12**, 236–254; *Ref. Zhur., Khim.*, 1961, (3), Abstr. No. 3D155.—*Procedure*—Place tungsten or molybdenum powder (50 mg) in the crater (diam. 4·5 mm, depth 5 mm) of a carbon electrode. Excite spectra by evaporation of the substance from the anode with a 7 amp. current and 2·5-mm gap. Photograph the spectra for 2 min. without pre-burning in a medium spectrograph; during this time only impurities are evaporated. Prepare standards by adding oxides or pure metals to pure tungsten or molybdenum. Construct calibration curves for the lines Cd 2288·0, Sb 2598·0, Pb 2833·1, Sn 2839·9 and Bi 3067·7. The background serves for comparison. The experimental error is 20%; the accuracy is within 10 p.p.m. To determine a lower concn., convert the sample into oxide, mix with carbon (3:1) and evaporate the impurities under vacuum from small graphite cups on to electrodes that are subsequently used in a high-voltage spark discharge. The sensitivity of a determination is 5 × 10^{-5} % for Pb, Bi and Cd, and ≃ 1 × 10^{-4} % for Sn and Sb.

K. R. COOK

3702. **Spectrographic determination of the oxygen and nitrogen content of molybdenum and chromium.** M. S. Alpatov, P. N. Galonov, K. A. Sukhenko and O. B. Fal'kova. *Trudy Komiss. Anal. Khim., Akad. Nauk SSSR*, 1960, **12**, 288–297; *Ref. Zhur., Khim.*, 1961, (3), Abstr. No. 3D154.—Determine O by a low-voltage pulse discharge in a helium atmosphere (700 torr), with the sample as cathode and a graphite pencil anode. Determine N by a low-voltage spark discharge in a helium atmosphere (700 torr), with the sample as cathode and a tungsten pencil anode. In chromium, O is determined in the range 0·005 to 0·2% and N in the range 0·009 to 0·15%; in molybdenum, the comparable ranges are 0·003 to 1% and 0·002 to 0·018%. The mean error is 25 to 55%.

K. R. COOK

3703. **Colorimetric determination of traces of silica in molybdenum and molybdenum compounds.** K. Fukker and A. J. Hegedüs (Forschungsinst. für die Nachrichtentech. Ind., Tungsram, Budapest, Hungary). *Mikrochim. Acta*, 1961, (2), 227–234 (in German).—The method described is a modification of that of Millner and Neugebauer (*Magyar Kém. Foly.*, 1951, **57**, 321). *Procedure*—Heat the sample (62 mg of MoO_3) in a platinum crucible with

10N-NaOH (0·19 ml) and water (2·3 ml) for 5 min. on a water bath. Add sodium molybdate soln. (82 g of MoO_3 and 39·4 g of NaOH in 1 litre) (10 ml) and adjust the soln. to pH 2 with 2N-HNO_3, with Tropaeolin OO (C.I. Acid Orange 5) as indicator. Dilute to 40 ml and place the flask in a water bath at 20° for 45 min. Add benzidine soln. (0·1% in 1% acetic acid) (1 ml) and 40% Na acetate soln. (3 ml), shaking vigorously between each addition. Replace in the water bath for a further 5 min., then measure the extinction at 570 mμ. The weight of MoO_3 taken for analysis can be increased to a maximum of 880 mg by using a larger vol. of 10N-NaOH and a smaller vol. of sodium molybdate soln. Molybdenum metal samples are converted into MoO_3 by evaporation with HNO_3 - H_2SO_4 on a sand bath. For up to 100 μg of SiO_2 the precision is $\simeq \pm 4\%$.

W. T. CARTER

3704. **Colorimetric determination of uranium(VI).** G. Baiulescu and I. C. Ciurea (Univ. I. C. Parhon, Bucharest, Romania). *Anal. Chim. Acta*, 1961, **24** (2), 152–154 (in English).—A 2% soln. of 4-(3-carboxy-4-hydroxyphenylazo)-3-methyl-1-phenylpyrazol-5-one in ethanol is used as a colorimetric reagent for U^{VI} in the concn. range 1·7 to 41 μg per ml. The pH of the soln. is adjusted to between 5 and 6 and a M53 filter is used with a Pulfrich photometer. H. N. S.

3705. **Comparison of some methods for the spectrophotometric determination of uranium(VI).** S. Ahrland (Eurochemic, Mol-Donk, Belgium). *Svensk Kem. Tidsskr.*, 1960, **72** (12), 757–762 (in English).—The following reagents for the determination of small amounts of U^{VI} are compared—thiocyanate in aq. soln., thiocyanate in ethanol soln., $K_4Fe(CN)_6$, $Na_4Fe(CN)_6$, and H_2O_2 in carbonate - hydroxide soln. The thiocyanate methods are found to be the best, being as rapid and accurate as the other methods, but suffering much less from interference by impurities likely to be present. The H_2O_2 method is inferior to the other methods.

P. PEDERSEN

3706. **Spectrographic determination of uranium-235. II. Using a direct-reading attachment and a hollow-cathode source.** T. Lee and L. H. Rogers (Tech. Div., Oak Ridge Gaseous Diffusion Plant, Union Carbide Nuclear Co., Tenn., U.S.A.). *Appl. Spectroscopy*, 1961, **15** (1), 3–6.—The sample is introduced as a uranyl nitrate solution into the removable hollow iron cathode, where it is dried. The emission from the demountable hollow-cathode discharge-tube is resolved in a 21-ft. Wadsworth grating spectrograph, giving 2·5 A per mm in the second order. A reciprocating scanning mechanism is described which, when used with an IP 21 photomultiplier tube as the receiver, gives a trace of the spectral region containing ^{238}U 4244·373 A and ^{235}U 4244·122 A. Calibration is by means of standard samples, and the precision is 1·2 to 1·8% of the amount present over the range 8 to 12% of ^{235}U in ^{238}U.

III. Use of a multiple hollow-cathode source assembly and a 22-ft. direct-reading Eagle spectrograph. T. Lee and S. A. MacIntyre. *Ibid.*, 1961, **15** (2), 34–39.—Limitations of earlier procedures (Lee *et al.*, *Ibid.*, 1960, **14**, 39; Lee and Rogers, *Anal. Abstr.*, 1961, **8**, 3706, Part II) have been overcome with a 22-ft. spectrograph, using 5 in. of a concave grating (15,000 lines per in.) in the second order to provide a resolution of 15×10^4 and an inverse linear dispersion of 1·33 A per mm. Samples are excited by radiation from four hollow-cathode discharge lamps and an adjustable selector mirror. A complete analysis in duplicate (including a close comparison of unknown and standard) can be made in < 20 min., with a minimum error from exit-slit misalignment and a minimum loss of time caused by the pre-burn period. The results obtained by this method for concn. of ^{235}U from 10 to 85% agree closely with those obtained by the mass spectrometer, whilst the error over the range of 30 to 40% of ^{235}U is ± 0·17% (65 samples). A weak U line at 42440·9 A still interferes with the measurements, especially at low concn. of ^{235}U; corrections for the effect of concn. of ^{234}U and ^{236}U are generally necessary.

P. T. BEALE
W. J. BAKER

3707. **Trace analysis [of uranium] by combination of ion exchange and X-ray fluorescence.** J. N. van Niekerk, J. F. de Wet and F. T. Wybenga (Nat. Phys. Res. Lab., S. African C.S.I.R., Pretoria). *Anal. Chem.*, 1961, **33** (2), 213–215.—A rapid and precise method is described for determining U in concn. as low as 0·1 p.p.m. The method involves concentration on Bio-Rad Ag-1X resin (SO_4^{2-} form) followed by direct determination on the resin by X-ray spectrography. The method is useful in routine control and reference analysis and compares favourably with current methods in rapidity and accuracy.

C. B. BAINES

3708. **Quantitative determination of uranyl ion by means of the uranyl-sensitised photo-decomposition of oxalic acid.** A. E. Taylor, G. E. Heckler and D. R. Percival (Idaho State Coll., Pocatello, U.S.A.). *Talanta*, 1961, **7** (3–4), 232–236 (in English).—The rate of catalysed decomposition of oxalic acid by u.v. light is proportional to the concn. of UO_2^{2+}, and the amount of gaseous product can be determined in a Warburg const.-vol. apparatus. The test is performed at pH 2·75, with a 2-min. exposure to u.v. light; variations in the flask - manometer assemblies are corrected by use of a reference system. Phosphate, F^- and Al^{3+} reduce the reaction rate, while Fe^{3+} enhance it. P. D. PARR-RICHARD

3709. **Sources of error in the polarographic determination of microgram amounts of uranium (after enrichment of solid samples and water).** P. Antal (Anal. Inst., Univ., Wien, Austria). *Mikrochim. Acta*, 1961, (2), 235–244 (in German).—Methods for the separation of U before its polarographic determination by the catalysis of the electrolytic reduction of NO_2^- in 0·01N-HNO_3 (Hecht *et al.*, *Anal. Abstr.*, 1957, **4**, 99) are reviewed. It is shown that polarographic difficulties associated with some methods of separation when used for the analysis of minerals are due to the presence of traces of Sn, Th, Mo, W, V, Nb, Ta and Pt. Alternative methods of separation are now available which eliminate the interference from this source. W. T. CARTER

3710. **Radiochemical determination of radium in uranium milling process samples.** H. G. Petrow and R. Lindstrom (Ionics, Inc., Cambridge, Mass., U.S.A.). *Anal. Chem.*, 1961, **33** (2), 313–314.—A recent method (Petrow *et al.*, *Ibid.*, 1960, **32**, 926) is modified to increase the sensitivity and accuracy and shorten analysis time. The amount of inert material accompanying the Ra is decreased by substituting ammonium carbonate for Na_2CO_3 as the reagent for the conversion of $PbSO_4$ into $PbCO_3$, and solvent extraction replaces the ion-exchange

step, Aliquat 336, a quaternary amine, being used as the extractant. The method is sensitive to 2 disintegrations per min. of Ra per litre provided that a 500-ml sample is taken. C. B. BAINES

3711. **Organic co-precipitants. XIII. Co-precipitation of quadrivalent plutonium.** V. I. Kuznetsov and T. G. Akimova. *Radiokhimiya*, 1960, **2** (3), 357–363; *Ref. Zhur., Khim.*, 1960, (21), Abstr. No. 84,437.—A method is developed for the pptn. of Pu from dil. soln., with separation from large amounts of other elements (other than U^{4+}, Th and Ce^{4+}), by co-pptn. (as a salt of $Pu(NO_3)_6^{2-}$) with a ppt. of the nitrate of rhodamine B butyl ester (butylrhodamine). To 200 ml of test soln. (containing $> 0{\cdot}01$ μg of Pu and < 500 mg of other elements) add NH_4NO_3 to a concn. of 50% and HNO_3 to a concn. of 1·8N, then slowly add 1 g of phenolphthalein and 40 ml of 1% **I** soln. Set aside for 1 hr., filter, wash the ppt. (× 2) with a soln. 50% in NH_4NO_3 and 1·8N in HNO_3 to which sufficient butylrhodamine has been added to give a slight ppt., transfer the ppt. and filter to a porcelain crucible, add 2 ml of conc. $(NH_4)_2SO_4$ soln. and ignite at 550° to 600°. Determine the Pu content radiometrically. Double pptn. is required for the separation of Pu from large amounts of U^{VI} (Pu:U = 1:10).
C. D. KOPKIN

3712. **Mercurimetric determination of chloride ion with a new indicator.** A. I. Zinov'ev and N. S. Solov'eva. *Trudy Vses. Nauch.-Issled. Geol.-Razved. Inst.*, 1960, (155), 325–328; *Ref. Zhur., Khim.*, 1960, (22), Abstr. No. 88,335.—The titration of Cl^- is carried out with $Hg(NO_3)_2$ soln., with a mixed indicator, diphenylcarbazone-bromophenol blue. If a yellow colour is obtained on adding the indicator to the test soln. add 0·05N-NaOH dropwise from a burette until a lilac colour appears, then neutralise with 0·05N-HNO_3 until the addition of one drop produces a yellow colour. If a lilac colour is obtained on addition of the indicator, neutralise with 0·05N-HNO_3. Titrate the soln. with 0·1N-$Hg(NO_3)_2$ to a lilac colour. The method is useful in the analysis of natural water. The accuracy compares favourably with that of the argentimetric method. K. R. COOK

3713. **An interpretation of the end-point error in the potentiometric titration of bromide and chloride mixtures with silver nitrate.** R. C. Bowers, L. Hsu and J. A. Goldman (Dept. of Chem., Northwestern Univ., Evanston, Ill., U.S.A.). *Anal. Chem.*, 1961, **33** (2), 190–194.—The bromide end-point error in the titration of mixtures of Br^- and Cl^- with $AgNO_3$ soln. can be minimised (1·2 to 1·5%, with equimolar concn. of Br^- and Cl^-) by adding sufficient electrolyte, *viz.* 80 mM-KNO_3 or 2·6 mM-$Ca(NO_3)_2$, to flocculate the AgBr as it forms. The extent of the error depends on the rate of addition of $AgNO_3$ soln. and the original ratio of Cl^- to Br^-. Any Cl^- in excess of that for ideal uniform mixed-crystal formation enters the AgBr and exchanges with Br^- in soln., only slowly during non-flocculating conditions, but very rapidly after flocculation. The distribution of Cl^- and Br^- between solid and soln. then approaches that required for ideal homogeneous mixed crystals. The error can be determined semi-quant. by assuming that the ratio of Cl^- to Br^- adsorbed on colloidal AgBr is proportional to the relative concn. of these ions in soln. and governs the relative amounts of these ions pptd. at any stage of the titration. These conclusions do not necessarily invalidate the findings of Kolthoff *et al.* (*J. Amer. Chem. Soc.*, 1939, **61**, 1036; 1954, **76**, 1503). W. J. BAKER

3714. **Precision null-point potentiometry. Direct micro-determination of iodide in solutions with high chloride concentrations.** H. V. Malmstadt and J. D. Winefordner (Dept. of Chem. and Chem. Engng, Univ. of Illinois, Urbana, U.S.A.). *Anal. Chim. Acta*, 1961, **24** (1), 91–96 (in English).—Micro amounts of iodide may be rapidly and accurately determined by this technique in the presence of a 2×10^5 excess of chloride. Brine and iodised-salt soln. containing respectively from 10 and 5 μg of iodide per ml were determined with an accuracy of ≃5%. A. C. R. HARTLEY

3715. **Polarographic determination of iodine in tellurium metal.** V. T. Athavale, R. G. Dhaneshwar, S. V. Gulavane and M. S. Varde (Anal. Div., Atomic Energy Estab. Trombay, Bombay, India). *Anal. Chem.*, 1961, **33** (2), 311–312.—The procedure described follows closely that developed by Miles *et al.* (A.E.R.E., Report I/R 1038, 1952), except that the final measurement is made polarographically instead of spectrophotometrically. The sample is oxidised with $K_2Cr_2O_7$ plus H_2SO_4 at 80°, oxalic acid is added, and the iodine is removed by distillation, absorbed in aq. NaOH, extracted into CCl_4, back-extracted into NaOH, and finally oxidised with Br in the presence of H_2SO_4. After the soln. has been concentrated by evaporation, the IO_3^- are determined polarographically at 30° with M-KCl and 0·05 M-$Na_2B_4O_7$ as supporting electrolyte. The $E_{\frac{1}{2}} = -1{\cdot}2$ V *vs.* the S.C.E. The recovery of iodine (1 to 10 μg) is >96%.
W. J. BAKER

3716. **Photometric determination of iodates.** S. S. Vil'borg and V. A. Drozdov. *Izv. Vyssh. Ucheb. Zavedenii, Khim. i Khim. Tekhnol.*, 1960, **3** (1), 75–77; *Ref. Zhur., Khim.*, 1960, (20), Abstr. No. 80,838.—The method consists in photometry of the soln. of ellagic acid formed when tannin (**I**) reacts with IO_3^- in acid medium. The max. colour intensity is at pH 2·56; the colour develops within 3 min. and does not change for 1·5 hr. To construct a calibration curve, to 15 ml of a 3% **I** soln. add standard iodate soln. (0·094 to 1·452 mg of IO_3^-) and 4 ml of 2N-acetic acid, make up to 50 ml, and after 3 min. measure the extinction in a 20-mm cell with a blue filter. The blank contains all these components except the oxidant. Beer's law is obeyed. C. D. KOPKIN

3717. **A special adaptation of the Volhard method for the analysis of manganese oxide ores.** V. L. Garik and L. M. Silber (Microwave Res. Inst., Polytech. Inst., Brooklyn, N.Y., U.S.A.). *Anal. Chem.*, 1961, **33** (2), 319–320.—A rapid modified Volhard method for determining Mn^{3+} and Mn^{4+} in, *e.g.*, impure oxides ($xMnO.yMnO_2$), is based on extraction of Mn^{3+} with warm dil. H_2SO_4 and concurrent disproportionation of Mn^{3+} into Mn^{2+} and Mn^{4+}. The content of Mn^{II} is determined by first adjusting an aliquot of the warm soln. to pH 7·5 to 8·0 with 4N-Na_2CO_3 and then titrating with MnO_4^- reagent to the nearest 0·5 ml (addition of the alkali advances the apparent end-point 2 to 3%, thus making it more readily seen); this vol. of titrant is then added to another aliquot, the soln. is adjusted to pH 7 ± 0·2 with HCl, and the titration is completed at 85° to 95° to the usual end-point. The concn. of MnO_2 (unaffected by the analytical

Izv. Vyssh. Ucheb. Zavedenii, Khim. i Khim. Tekhnol., 1960, **3** (1), 72–74; *Ref. Zhur., Khim.*, 1960, (20), Abstr. No. 80,782.—Conditions are studied for the formation of the complex of Zr^{IV} with 4,5-dihydroxy-3-(*p*-sulphophenylazo)naphthalene-2,7-disulphonic acid (**I**). The reaction is best carried out in 5N-$HClO_4$, with photometry of the resulting soln. at 580 mμ after reducing the pH to between 0·9 and 1·1, with 0·1% aq. **I** soln. as comparison soln. The stability of the complex with time depends on the acidity of the original soln. of Zr^{IV}, the complex being more stable if formed in 9N-$HClO_4$, but after reducing the pH to 1 its light absorption is less than that of the complex obtained in 5N-$HClO_4$. The mol. extinction coeff. at 580 mμ is 18,900; Beer's law is obeyed at concn. of 4 to 40 μg of Zr in 25 ml. The sensitivity of the method is 0·02 μg per ml. The ratio of Zr to **I** in the complex is 1:2. The difference between the results obtained and literature data is due to the different acidities of the soln. in which the complex is formed.

C. D. KOPKIN

3660. **Gravimetric determination of zirconium(IV) with Orange II.** G. Baiulescu and A. Kriza (Lab. de Chim. anorg. şi Anal., Fac. Chim., Univ. "C.I. Parhon," Bucureşti). *Acad. R.P.R., Stud. Cercet. Chim.*, 1960, **8** (3), 541–543.—The acidified soln., containing about 0·2% of Zr, is heated nearly to boiling and an excess of aq. 1% Orange II (C.I. Acid Orange 7) (sodium salt) soln. is added. The ppt. is filtered off, washed with hot water, ignited, and weighed as ZrO_2. If the test soln. is 0·75N in HCl, quant. pptn. may be effected even when the ratio of U to Zr is 220:1. D. R. DUNCAN

3661. **Determination of small amounts of zirconium in ores.** L. I. Kononenko and N. S. Poluéktov. *Trudy Komiss. Anal. Khim., Akad. Nauk SSSR*, 1960, **12**, 132–141; *Ref. Zhur., Khim.*, 1960, (24), Abstr. No. 96,129.—Two photometric methods are developed for the determination of Zr in ores, with arsenazo (**I**) and Alizarin red S (C.I. Mordant Red 3) (**II**). Tervalent Fe is first reduced to Fe^{II} with hydroxyammonium chloride. To remove interference due to Ti, Nb, Mo and Sn when using **I**, and Ta, Ti, Nb and Mo when using **II**, the extinctions of the test soln. with **I** or **II** are measured against the same blank containing EDTA (disodium salt), which selectively masks Zr and does not react with the coloured complexes of the other elements. For the direct determination of Zr in ores (0·1 to 2·0% of ZrO_2), decompose 0·1 g of sample by fusion with a mixture of $Na_2B_4O_7$ and Na_2CO_3, dissolve the melt in water, filter, and wash the pptd. hydroxides; dissolve them in HCl, and determine Zr in an aliquot of the soln. To determine smaller contents of Zr (0·005 to 0·01% of ZrO_2), precipitate Zr as the phenylarsonate in the presence of H_2O_2 from a soln. prepared as described above from a larger sample (0·5 g), filter off the ppt., decompose it on the filter with aq. NH_3, add $AlCl_3$ (3 mg of Al) to the filtrate to precipitate the partially dissolved Zr with the $Al(OH)_3$, and filter through the same filter. Dissolve the ppt. in HCl, extract Zr from the filtrate with oxalic acid soln., destroy oxalic acid with $KMnO_4$ and determine Zr photometrically with **I** or **II**. The completeness of separation of Zr was tested by means of the radioactive isotope ^{181}Hf and found to be 94 to 97%. The results of determining 0·02 to 0·2% of Zr in ores agree well with those of the emission spectrographic method. C. D. KOPKIN

3662. **Anion-exchange studies of zirconium(IV) in citrate solution. Separation from mixtures.** Shripad M. Khopkar and Anil K. De (Jadavpur Univ., Calcutta, India). *Anal. Chim. Acta*, 1961, **24** (2), 134–137 (in English).—The citrate complex of Zr is retained on a column of Dowex 21K anion-exchange resin from a soln. buffered at pH 2·7 to 3·0 with ammonium citrate, and is thus separated from Pb and the fission-product elements Ba, Sr, Cd, Cs and Mo. The Zr is eluted with HCl (0·5N to 2N), the citrate is destroyed with HNO_3 and $HClO_4$, and the Zr is determined as oxide. Antimony, Th, U and V interfere. H. N. S.

3663. **Separation of hafnium from zirconium by anion exchange.** J. L. Hague and L. A. Machlan (Nat. Bur. of Standards, Washington, D.C., U.S.A.). *J. Res. Nat. Bur. Stand., A*, 1961, **65** (1), 75–77.—Hafnium and Zr (≃100 mg of each) can be effectively separated by adsorption as SO_4^{2-} complexes on a strong quaternary amine anion-exchange resin, followed by elution (flow rate 100 ml per hr.) with ≃1 litre of 3·5% H_2SO_4. The initial eluate contains Hf with 10 to 100 p.p.m. of Zr, the next fraction (≃150 ml) contains neither element, and the final eluate contains Zr with 10 to 100 p.p.m. of Hf. The resin bed (7·5 in. high) consists of Dowex 1 (<270 mesh) containing 8% of divinylbenzene cross-linkages. Elution with a mixture of HCl and H_2SO_4 is unsatisfactory. W. J. BAKER

3664. **Spectrographic analysis of hafnium by a point-to-plane technique.** R. C. Brayer, R. F. O'Connell, A. S. Powell and R. H. Gale (Combustion Engng, Inc., Nuclear Div., Mat. Dev. Lab., Windsor, Conn., U.S.A.). *Appl. Spectroscopy*, 1961, **15** (1), 10–13.—An ignited a.c. arc is used for the excitation of solid metallic samples with a graphite counter-electrode. A 3·4-metre Ebert Jarrell-Ash grating spectrograph with 15,000 lines per inch gives sufficient dispersion, and suitable lines are identified in the region 2800 to 3400 A for the determination of Zr (1 to 4%), Al (20 to 150 p.p.m.), Cu (5 to 150 p.p.m.), Fe (20 to 500 p.p.m.), Ti (10 to 100 p.p.m.) and W (20 to 500 p.p.m.), with Hf 2951·9 A as the internal-standard line. Calibration was by means of chemically analysed samples. The reproducibility was satisfactory and comparisons with chemical analyses on buttons melted from hafnium sponge material are reasonable, although discrepancies are shown in the chemical analyses carried out by different laboratories. P. T. BEALE

3665. **Analytical chemistry of thorium—a bibliography.** M. R. Verma, Jitendra Rai and Prabhu Dayal (Nat. Phys. Lab., New Delhi). *J. Sci. Ind. Res., India, A*, 1961, **20** (2), Suppl. 1–24; **20** (3), Suppl. 25–46.—A bibliography of 902 references published from 1940 to 1958 inclusive is presented.

3666. **Detection of thorium with Alizarin red S and its determination with the Weisz ring-oven.** L. Hainberger and S. Cuadrado Sanchez (Inst. de Quím. Pontifícia Univ. Católica, Rio de Janeiro, Brazil). *Mikrochim. Acta*, 1961, (2), 245–249 (in German).—Thorium hydroperoxide forms a purple complex with Alizarin red S (C.I. Mordant Red 3) which can be used for the detection of 0·05 μg of Th in neutral soln. The reagent is 0·1% aq. Alizarin red S soln. containing 10% of NH_4NO_3 and 15% of H_2O_2. The reaction is not specific, and samples containing other metals, *e.g.*, minerals, must be subjected to a separation procedure in which the sample is fused with solid NaOH, acidified

with HNO_3, and made alkaline with aq. NH_3. Thorium is pptd. as the fluoride with excess of NaF and converted into the hydroxide with aq. NH_3; this is dissolved in HNO_3 containing $Al(NO_3)_3$ and extracted into tri-n-butyl phosphate in xylene. Finally the Th is re-extracted into water and subjected to the spot test or determined quantitatively with the ring-oven. W. T. CARTER

3667. **Spectrophotometric determination of traces of boron in thorium.** Hiroshi Onishi, Nasumi Ishiwatari and Hitoshi Nagai (Japan Atomic Energy Res. Inst., Tokai, Ibaraki-ken). *Bull. Chem. Soc. Japan*, 1960, **33** (12), 1686–1688.—The sample (thorium oxide or metal) is dissolved in conc. H_3PO_4, the soln. is diluted with water, the B is separated by distillation as trimethyl borate, and determined by the curcumin method (*Ibid.*, 1960, **33**, 830). The error is $\pm 0{\cdot}1$ p.p.m. for 0·2 to 1·0 p.p.m. of B. I. JONES

3668. **Recovery of radioactive thorium indicator on an ion-exchange resin.** A. M. Petrov, I. A. Korshunov and V. A. Sidorov. *Trudy Khim. i Khim. Tekhnol.*, 1959, (3), 498–499; *Ref. Zhur., Khim.*, 1961, (3), Abstr. No. 3D81.—The isotope ^{234}Th is separated from U-containing soln. by addition of hydroxylamine, to give the anionic complex of U, and passage through the cation-exchange resin KU-1. The small amount of adsorbed U is eluted with 0·5N-HCl, and the ^{234}Th is then eluted with 4N-HCl. K. R. COOK

3669. **Determination of hydrazoic acid and ferric ion by spectrophotometric measurement of the ferric azide complex.** E. K. Dukes and R. M. Wallace (Savannah River Lab., E. I. du Pont de Nemours & Co., Inc., Aiken, S.C., U.S.A.). *Anal. Chem.*, 1961, **33** (2), 242–244.—The three procedures given permit the determination, either separately or simultaneously, of HN_3 and Fe^{3+} in soln. of HNO_3 containing hydrazine, Fe^{3+}, Fe^{2+} and HN_3. (*i*)—If either HN_3 or Fe^{3+} are present, a known vol. of 0·5M-$Fe(NO_3)_3$ or NaN_3, respectively, is added to the sample soln. and, after diluting the mixture, the concn. of HNO_3 is determined by titration with NaOH soln. (any Fe^{3+} must be complexed with oxalate). The extinction of the ferric azide complex is then measured at 460 mμ and 23° against a reagent blank. (*ii*)—If Fe^{3+} and HN_3 are both present, but in concn. insufficient to give a measurable extinction, the same procedure can be used, but the concn. of the added component must be very high or the acidity must be reduced. (*iii*)—If Fe^{3+} and HN_3 are both present in sufficient concn. to produce a measurable extinction, an aliquot of the sample soln. is diluted with 0·5M-HNO_3 and the extinction of the ferric azide complex is measured. A known concn. of either Fe^{3+} or HN_3 is then added to another aliquot similarly diluted, and the increased extinction is measured. In all three procedures the concn. of Fe^{3+} and HN_3 are calculated from equations, taking into account the concn. of HNO_3. The standard deviation is 0·0016 (10 analyses for molarities from 0·0075 to 0·305); max. sensitivity is attained at low concn. of HNO_3. Max. concn. of 0·25M-Fe^{3+} and 0·12M-HN_3 were used. W. J. BAKER

3670. **The absorption spectrum of nitrous acid in tributyl phosphate, and its application to analyses for nitrous acid.** J. Woodhead (Chem. Div., A.E.R.E. Harwell, England). A.E.R.E. Report R 3432, 1960. 10 pp.—Concn. of NO_2^- as low as 5×10^{-4}M can be determined accurately by stirring an aliquot of the aq. soln. for 5 min. with a known vol. of 20 to 100% (v/v) tributyl phosphate soln. in kerosine (previously equilibrated with 0·25M-$HClO_4$), adjusting the acidity to $<0{\cdot}5$M with either H_2O or $HClO_4$. The mixture is centrifuged, the spectrum of the organic phase is recorded between 320 and 400 mμ and the concn. of NO_2^- is then calculated from the molar extinction coeff. for the peaks at 375·5 and 390·5 mμ. When other extractable species are present the organic phase must be washed three times with twice its vol. of H_2O before recording the spectrum. Beer's law is followed over the range 0·0005 to 0·01M-NO_2^-.

3671. **Rapid method for the determination of ammonia (combined) and phosphate in the system of diammonium phosphate and dipotassium phosphate.** B. Paschkes and B. Bernas (Israel Mining Industries Lab., Haifa, Israel). *Anal. Chim. Acta*, 1961, **24** (1), 5–10 (in English).—*Procedure*—The PO_4^{3-} ($\simeq 60$ mg) are determined in one 50-ml aliquot of sample soln. by direct titration with 0·1N-HCl, with methyl orange as indicator. Excess of 0·1N-NaOH is added to a second aliquot of sample soln., and NH_3 ($\simeq 15$ mg) is removed by boiling. Titration of the cooled soln. with 0·1N-HCl, with methyl orange as indicator, gives the sum of PO_4^{3-} and unchanged NaOH. The content of NH_3 may be deduced from the difference between the two titrations. A. C. R. HARTLEY

3672. **Separation of phosphate ion from arsenate ion by solvent extraction.** H. H. Ross and R. B. Hahn (Dept. of Chem., Wayne State Univ., Detroit, Mich., U.S.A.). *Talanta*, 1961, **7** (3–4), 276–280 (in English).—Various solvents and solvent mixtures were studied as selective extractants for PO_4^{3-} from soln. containing AsO_4^{3-}. Butanol - $CHCl_3$ was the most promising system; the amounts of PO_4^{3-} and AsO_4^{3-} extracted by a 4:1 mixture were 94·97 and 4·7%, respectively. Addition of PO_4^{3-} did not significantly reduce the extraction of AsO_4^{3-} at this solvent ratio. P. D. PARR-RICHARD

3673. **The evolution of arsine from alkaline solution.** A. J. Hegedüs and M. Dvorszky (Forschungsinst. für die Nachrichtentech. Ind., Tungsram, Budapest, Hungary). *Mikrochim. Acta*, 1961, (2), 186–190 (in German).—The amount of AsH_3 evolved from alkaline soln. depends on the alkalinity of the soln. and the purity, activity, and dimensions and nature of the surface of the aluminium used for the reduction. Recoveries of 95 to 100% are obtained for 100 μg of As with 0·5N-KOH and aluminium filings (99·99% purity) activated immediately before use by immersion in 0·1N-KOH containing 0·5 p.p.m. of As. Quinquevalent As is not reduced under the conditions of the test, and a prior reduction in acid soln. is necessary. In soln. containing W, this causes the pptn. of tungstic acid, which adsorbs the As. W. T. CARTER

3674. **Sources of error in the volumetric microdetermination of arsenic by the method of Bodnár, Szép and Cieleszky.** A. J. Hegedüs and M. Dvorszky (Forschungsinst. für die Nachrichtentech. Ind., Tungsram, Budapest, Hungary). *Mikrochim. Acta*, 1961, (2), 181–185 (in German).—Low results in this method (*cf. Z. anal. Chem.*, 1939, **115**, 412) are caused by the presence of cyanate in the KCN used in the titration, impurities in the tin used for the generation of AsH_3, the formation of As_2O_3 in the heated silica tube, the presence of traces of

oxidising agents in the reagents and the existence of unfavourable equilibria in some of the reactions.
W. T. CARTER

3675. **Volumetric micro-determination of traces of arsenic in tungsten, molybdenum and other metals.** A. J. Hegedüs and M. Dvorszky (Forschungsinst. fur die Nachrichtentech. Ind., Tungsram, Budapest, Hungary). *Mikrochim. Acta*, 1961, (2), 169–180 (in German).—The modified Marsh test of Bodnár *et al.* (*Z. anal. Chem.*, 1939, **115**, 412) is applied to the determination of traces of As in tungsten and tungstic oxide. Tungstic oxide is analysed directly after being dissolved in alkali. Metallic tungsten is converted into WO_3 by slow oxidation at 600° or by dissolution in HNO_3, H_3PO_4, or HNO_3 - H_3PO_4 - H_2O_2. By using an empirical factor obtained by calibration with soln. of known As content, an accuracy of $\pm 2{\cdot}3\%$ can be achieved for $\simeq 70$ μg of As in 1 g of tungsten. The method can also be used for the determination of As in metallic molybdenum, zinc, sodium, copper, lead, magnesium, barium, manganese, iron, aluminium, calcium and mercury. W. T. CARTER

3676. **Polarographic analysis using potassium iodide as supporting electrolyte. III. Polarographic behaviour of tervalent arsenic.** Teiichi Matsumae and Ryozo Nakashima (Govt. Ind. Res. Inst., Nagoya, Japan). *Anal. Chim. Acta*, 1961, **24** (2), 192–199 (in English).—Tervalent As yields two polarographic waves in 0·1M-KCl. The effects of the height of the mercury column, temp. and pH are investigated. The sum of the wave heights bears a linear relationship to the concn. of As^{3+} at concn. < 0·004M and at pH 1·9 to 2·5. Dodecyltrimethylammonium chloride (0·001%) is used as max. suppressor. H. N. S.

3677. **Photometric determination of antimony with methylfluorone.** S. Meyer and O. G. Koch (Chem. Lab., Neunkircher Eisenwerk A.-G., Neunkirchen, Saar). *Z. anal. Chem.*, 1961, **179** (3), 175–186 (in German).—To prepare the reagent, dissolve methylfluorone (2,6,7-trihydroxy-9-methylfluorone) (0·05 g) in 2N-NaOH (5 ml), add water (25 to 30 ml), ethanol (50 ml) and, with cooling, conc. HCl (1·6 ml) and dilute to 100 ml with water. *Procedure*—To the test soln. ($\simeq$ N in HCl and containing 5 to 100 μg of Sb) add Clark and Lubs buffer soln. (pH 2) (5 ml), 1% poly(vinyl alcohol) soln. (1 ml) and reagent (1 ml). Dilute to $\simeq$40 ml, adjust the pH to 2·0 with 2N-NaOH or 2N-HCl, dilute to 50 ml with water and measure the extinction at 495 mμ against water. Subtract the extinction of a reagent blank. Beer's law is obeyed over the range 0·2 to 4·0 μg of Sb per ml. Determinations of 1 μg of Sb per ml gave a standard deviation of $\pm$ 0·018. The reaction of 53 other cations with the reagent and the influence of 25 anions on the reaction are recorded.
A. J. BENNETT

3678. **New colour reaction for the detection of stibine.** G. Ciuhandu and M. Rocsin (Inst. de Igienă, Lab. de Toxicol., Timişoara, Romania). *Acad. R.P.R., Stud. Cercet. Chim.*, 1960, **8** (3), 537–539.—Stibine in the gas obtained by reducing with nascent H a soln. containing as little as 1 g of Sb in 5 ml may be detected by the greyish-yellow to brown colour produced on passing the gas through 5 ml of an alkaline soln. of Ag *p*-sulphamoylbenzoate, prepared by mixing 1 vol. of 0·1M-Na-*p*-sulphamoylbenzoate with 1 vol. of 0·1M-$AgNO_3$ and adding 0·5 vol. of M-NaOH. D. R. DUNCAN

3679. **Separations involving sulphides. I. Separation of quinquevalent antimony from alkaline earths.** G. B. S. Salaria (Chem. Dept., Govt. Coll., Dharmsala, India). *Z. anal. Chem.*, 1961, **179** (2), 91–92 (in English).—The method previously described (*Anal. Abstr.*, 1959, **6**, 2459) has been extended to include antimony. T. R. ANDREW

3680. **Liquid - liquid extraction of vanadium(V) with tributyl phosphate.** Santosh K. Majumdar and Anil K. De (Jadavpur Univ., Calcutta, India). *Anal. Chem.*, 1961, **33** (2), 297–299.—Approx. 25 mg of V^V can be extracted (98 to 99% recovery) as $VOCl_3$.2(solvent) from 5N to 6N-HCl with 100% tributyl phosphate in $\simeq$5 min. After back-extraction into H_2O, the V can be determined volumetrically. None of the following ions interferes—Cu^{2+}, Hg^{2+}, Co^{2+}, Ni^{2+}, Ba^{2+}, Bi^{3+}, Fe^{3+}, Cr^{3+}, Th^{4+}, U^{6+}, Mo^{6+}, PO_4^{3-} and $EDTA^{4-}$, although Cu^{2+}, Co^{2+}, U^{6+}, Fe^{3+}, Th^{4+} and Mo^{6+} are co-extracted with the V. Citrate and tartrate must be absent.
W. J. BAKER

3681. **Study of the co-precipitation of vanadyl ions with aluminium hydroxide.** V. L. Zolotavin and Yu. I. Sannikov. *Trudy Ural'sk. Politekh. Inst.*, 1959, (8), 228–233; *Ref. Zhur., Khim.*, 1960, (20), Abstr. No. 80,700.—The pH values at which $Al(OH)_3$ and $VO(OH)_2$ begin to precipitate from pure soln. and when both are present are determined. Complete co-pptn. of VO^{2+} with $Al(OH)_3$ occurs when the relative content of V is $\geq$ 15%. It is suggested that the main process in the co-pptn. is the formation of a solid solution. The VO^{2+} are strongly held in the ppt., are not converted into hypovanadate and are not oxidised. The co-pptn. method enables the sensitivity of qual. reactions for V to be increased. C. D. KOPKIN

3682. **Determination of small amounts of vanadium in ores.** E. Pavlíková (Inst. Res. Ores, Prague). *Sb. Prac. Ust. Pro Výzk. Rud III*, 1958–59, 242–248.—A photometric tungstovanadophosphate method is described. Iron, Ni, Co, Mn, Cr, Sn, Bi, Sb and Mo are removed by mercury electrolysis, and any residual Ti is masked with NaF. The method is suitable for samples containing 0·001% of V. *Procedure*—Heat the finely powdered sample (0·5 to 3 g) with a mixture of equal vol. of HNO_3 (1:1) and H_2SO_4 (1:1) (20 to 25 ml). Evaporate to dryness, add H_2O, heat, filter and wash. If necessary, remove SiO_2 by the usual method. Evaporate the filtrate to $\simeq$80 ml and electrolyse for 1 hr. Then oxidise V^{IV} with bromine water, heat and transfer to a 50-ml flask and make up to vol. To an aliquot in a 25-ml flask add HCl (1:1) (0·5 ml), H_3PO_4 (1:2) (5 ml) and 0·25M-Na_2WO_4 (1 ml). Dilute with H_2O to vol., mix, and after 15 min. measure the extinction with violet filter S42. J. ZÝKA

3683. **Gravimetric determination of niobium as 8-hydroxyquinolinate.** A. A. Mambetov and N. A. Pzaeva. *Azerbaidzh. Sel.-Khoz. Inst.*, 1960, **11**, 221–227; *Ref. Zhur., Khim.*, 1960, (22), Abstr. No. 88,299.—*Procedure*—Fuse the sample with a 40-fold amount of $K_2S_2O_7$ in a quartz dish at 700° to 800° and leach with 20% tartaric acid soln. (40 to 50 ml). Dilute the soln. so as to obtain a tartaric acid content of 1 to 2 g and an Nb_2O_5 concn. of 20 to 50 mg in 100 to 120 ml, neutralise with aq. NH_3 to a pH of 4 to 7, heat to 70° to 80°, precipitate with a 2 to 3-fold excess of 3% ethanolic 8-hydroxyquinoline soln. and boil for 30 min. Allow the

ppt. to settle (15 to 20 min.), collect it in a sintered glass crucible (No. 4), wash it free from 8-hydroxyquinoline with warm H_2O and dry it at 110° to 115°.
K. R. Cook

3684. **Quantitative spectrographic determination of niobium in carbonaceous samples with pneumatic introduction of powders into the arc discharge.** R. S. Rubinovich. *Inform. Byull. Inst. Geol. Arktiki*, 1959, (16), 61–68; *Ref. Zhur., Khim.*, 1960, (21), Abstr. No. 84,454.—The substance is blown directly upwards from a special vessel into the arc gap between two horizontal carbon electrodes [*Ref. Zhur., Fiz.*, 1960, (7), Abstr. No. 18,613]; 3 to 4 mg of sample are blown into the discharge (current strength 16 to 18 amp.) in 15 sec. Samples and standards are first mixed with an equal amount of carbon powder to which Mo is added. The values of ΔS for the lines Nb 2950·9 and Mo 2934·3 A change during the blowing process, because of fractionation of particles according to their size, thus producing large errors. For smooth delivery of particles of various sizes, the samples and standards are treated with HF (to 0·2 g of sample add 20 mg of acid and evaporate at 200° for 1 hr.). Calibration curves constructed from standards on various bases do not coincide but, by allowing for the background, the graphs can be made to agree to within ± 10%. The results for a large number of determinations agree well with those by chemical analysis. The error is ≃ ± 7%.
C. D. Kopkin

3685. **Precipitation and determination of tantalum and niobium from homogeneous solution with 3,3′,4′,5,7-pentahydroxyflavanone.** F. L. Chan (Aeronaut. Res. Lab., Wright-Patterson Air Force Base, Ohio, U.S.A.). *Talanta*, 1961, **7** (3–4), 253–263 (in English).—On heating 3,3′,4′,5,7-pentahydroxyflavanone (**I**) in 6 to 9N acid soln., the corresponding flavone, which quant. precipitates Ta and Nb, is slowly generated. *Procedure for Ta or Nb*—Fuse the sample (> 20 mg of the oxide of Ta or Nb) with 1 g of $KHSO_4$, cool and extract the melt with hot conc. H_2SO_4 (5 × 5 ml). Cool the extract and pour it into 30 ml of satd. ammonium oxalate soln. to give a clear soln. Add a hot soln. of **I** (0·5 to 1·5 g of **I** in 45 ml of H_2O) and boil for 1 hr. (15 hr. for Nb). Add H_2O (50 ml) and set aside for 1 hr.; filter, and wash the ppt., first with 1% **I** soln. in N-H_2SO_4 (4 × 5 ml) and then with satd. aq. **I** soln. (6 × 5 ml). Ignite the paper and ppt. in platinum to const. wt. The separation of Ta and Nb is also described. Titanium should be absent.
P. D. Parr-Richard

3686. **Determination of mixed tantalum and niobium pentoxides.** Sh. G. Melamed, A. K. Rusanov and M. G. Zemskova. *Trudy Komiss. Anal. Khim., Akad. Nauk SSSR*, 1960, **12**, 65–70; *Ref. Zhur., Khim.*, 1961, (3), Abstr. No. 3D84.—For mixtures of the pentoxides containing 5 to 99% of Ta_2O_5, a spectrographic pressed-pellet technique, with a multisource discharge, is used. For Ta_2O_5 contents of <5% or Nb_2O_5 contents of <1%, a 10-amp. d.c. discharge is used. Titanium (>3%) interferes, but may be corrected for. Full analytical details are given, including precisions attained and details of the preparation of standards.
K. R. Cook

3687. **Use of phenylarsonic acid in turbidimetry. Determination of tantalum.** R. Saint-James and T. Lecomte (Centre d'Études Nucléaires de Saclay, Dépt. de Métall., Service A.R.C.A., Gif-sur-Yvette, Seine et Oise, France). *Anal. Chim. Acta*, 1961, **24** (2), 155–160 (in French).—The Ta content (0·2 to 2%) of uranium - tantalum alloys is determined with a relative error of < ± 0·5%. The turbidity developed on adding phenylarsonic acid soln. to a soln. of the sample in 2N to 3N-H_2SO_4 is stabilised by the addition of glycerol, and the extinction is determined at 350 mμ, with the application of appropriate blank corrections. An equiv. atomic concn. of Nb is tolerated if H_2O_2 is present. Zirconium interferes at an atomic ratio of Zr to Ta of > 5:1. Iron, if present, is reduced with ascorbic acid.
H. N. S.

3688. **Volumetric determination of sulphate ion.** B. A. Ryazanov. *Nauch. Trudy Mosk. Tekhnol. Inst. Legkoĭ Prom.*, 1960, (16), 62–65; *Ref. Zhur., Khim.*, 1960, (24), Abstr. No. 96,153.—A method is proposed for the direct titration of SO_4^{2-} in soln. of $Cr_2(SO_4)_3$ or $Al_2(SO_4)_3$ with $Pb(NO_3)_2$ soln., with dithizone as indicator. To a known vol. (10 to 20 ml) of soln. add 3 ml of ≃0·1N-HCl, 15 ml of acetone and 10 drops of a satd. soln. of dithizone in 100% acetone, and titrate slowly, with continuous stirring, with ≃0·1N-$Pb(NO_3)_2$ till the dithizone colour changes from green to red. Towards the end of the titration, add the $Pb(NO_3)_2$ soln. dropwise, shaking and allowing the soln. to stand for ≃1 min. The titration must be carried out in daylight. Titrating to a pink ppt. gives a result low by 4·32%, and to a bright-red ppt. a result high by 1·9%. With 29 to 76 mg of SO_4^{2-} the error was 0·63 to 0·99%.
C. D. Kopkin

3689. **Indirect determination of sulphate by non-aqueous titrimetry.** G. Goldstein, O. Menis and D. L. Manning (Anal. Chem. Div., Oak Ridge Nat. Lab., Tenn., U.S.A.). *Anal. Chem.*, 1961, **33** (2), 266–268.—From 1 to 6 mg of SO_4^{2-} in an aliquot of the aq. soln. can be determined, in the presence of such normally interfering ions as UO_2^{2+} and Fe^{3+}, by pptn. with an excess of 0·05N-Ba acetate, the excess of which is determined by potentiometric titration with 0·03N-$HClO_4$ in glacial acetic acid. The H_2O is eliminated by the addition of acetic anhydride (6 ml per ml of soln.) and boiling the mixture for ≃2 min.; addition of ≃10 ml of glacial acetic acid at the same time prevents pptn. of inorg. salts other than $BaSO_4$. Co-pptn. effects and minor cationic or anionic interferences are discussed. The precision is within 1% and the accuracy is equiv. to that for the cation exchange - $BaCl_2$ method. The procedure is suitable for the determination of total SO_4^{2-} in soln. of reactor fuels.
W. J. Baker

3690. **Determination of small amounts of selenium in anodic copper.** A. I. Zelyanskaya and L. S. Gorshkova. *Trudy Inst. Metallurg. Ural'sk. Fil. Akad. Nauk SSSR*, 1960, (5), 137–139; *Ref. Zhur., Khim.*, 1960, (24), Abstr. No. 96,154.—The method is based on the removal of Se from Cu by cation exchange, with subsequent determination of Se by iodimetric titration. Dissolve 2 g of the anodic copper in HNO_3 (1:1), evaporate the soln. with H_2SO_4, and add 225 ml of water (to dissolve the salts), 0·1 to 0·2 g of citric acid crystals (to complex Fe) and 25 ml of conc. aq. NH_3. Pass the resulting soln. at a rate of 6 to 8 ml per min. through a column (60 cm × 2·5 cm in diam.) packed with a 45-cm layer of Wofatit R (NH_4^+ form), which retains only the cuprammonium complex. Wash the column with aq. NH_3 (1:9), evaporate the percolate and wash soln. to 150 to 200 ml, neutralise

with HCl to Congo red, add excess of HCl (15 ml), a known vol. of standard $Na_2S_2O_3$ soln. and 2 to 3 ml of 1% starch soln., and titrate the unchanged $Na_2S_2O_3$ with iodine. The method has been used successfully to determine 0·011 to 0·039% of Se in industrial samples of anodic copper.

C. D. KOPKIN

3691. **Determination of selenium in sludge containing platinum.** V. I. Murashova. *Trudy Ural'sk. Politekh. Inst.*, 1960, **94**, 161–167; *Ref. Zhur., Khim.*, 1960, (22), Abstr. No. 88,332.—Treat the sludge (0·5 g) by heating with conc. HNO_3 (25 to 30 ml), add Na_2CO_3 until the first appearance of a hydroxide ppt., and then 20% NaOH soln. (20 ml), and hydroxyammonium chloride (**I**) (4 g). Boil for 2 to 3 min., cool, dilute to 100 ml and filter off the residue (Pt and Pd) with a dry filter. Neutralise the filtrate (50 ml) to litmus, add conc. HCl (5 mg per 100 ml of soln.) and urea (2 g), boil for 1 to 2 min., add **I** (5 g) and boil for another 15 min. Filter off the residue (Se), wash it with hot HCl (1:20), dissolve the ppt. by heating in conc. HCl (10 ml) plus conc. HNO_3 (6 drops), dilute, add urea and determine Se^{4+} iodimetrically. The error is 2%.

K. R. COOK

3692. **Indirect potentiometric method for the micro-determination of selenium.** H. Hahn and H. Bartels (Chem. Inst., Univ. Würzburg, Germany). *Mikrochim. Acta*, 1961, (2), 250–261 (in German).—The method of Hahn and Viohl (*cf. Anal. Abstr.*, 1956, **3**, 2069) is adapted to the determination of micro amounts of Se by using the procedure for the potentiometric titration of micro amounts of Ag^+ developed by Shiner and Smith (*Anal. Abstr.*, 1956, **3**, 3037). To obtain accurate results it is necessary to destroy excess of hydrazine by heating at 105° for 15 min. before the titration. Since very dilute soln. of $AgNO_3$ are photo-sensitive, it is essential to work in red light. The accuracy ranges from $\simeq \pm 2\%$ for 1 μg of Se to $\pm 1\%$ for 100 μg of Se. A twofold excess of Te does not interfere.

W. T. CARTER

3693. **Spot detection and quantitative determination of selenium and tellurium.** I. M. Korenman, V. G. Ganina and N. V. Kurina. *Trudy Khim. i Khim. Tekhnol.*, 1959, (2), 369–375; *Ref. Zhur., Khim.*, 1960, (23), Abstr. No. 92,080.—The reduction of selenites and tellurites is used for the detection and determination of elementary Se and Te. The best reducing agents are thiourea and hydroxyammonium chloride for selenites, and $SnCl_2$ for tellurites. When Na_2SeO_3 is treated with thiourea in the cold or with hydroxyammonium chloride with heating, a red ppt. or pink colour is formed, depending on the Se content. The detectable minimum of Se is 5 μg per ml at a limiting concn. of 1 in 2×10^5. The sensitivity of the reaction is increased five times by flotation of the elementary Se with ether, which is more suitable for this purpose than $CHCl_3$ or dichloroethane. Interference in the detection of Se is caused by Au, Pt and Pd, which are also reduced to metals in acid and alkaline media. No interference is caused by Co, Al, Bi, Ni, Pb, Cu or Ag. When K_2TeO_3 is treated with 10% $SnCl_2$ soln. in the cold, a black ppt. or brown colour is formed, depending on the Te content. The detectable minimum for Te is 10 μg per ml at a limiting concn. of 1 in 10^4. No interference in the detection of Te is caused by 100-fold amounts of Fe, Al, Bi, Co, Cu, Ni, Mg, Ba, Pb or Ag. The interference of H_2SeO_3 is removed by the action of thiourea, which reduces H_2SeO_3 to Se, leaving unchanged H_6TeO_6 in soln. Gold is pptd. with NaOH soln. in the presence of hydroxyammonium chloride. Procedures are given for determining Se with thiourea in the presence of other ions. The standard-series method can be used to determine 20 to 100 μg of Se per ml, and the nephelometric method for 2·5 to 25 μg of Se per ml, with mean errors of 5% and 1%, respectively. Tellurium can be determined with $SnCl_2$ in the presence of other ions by the nephelometric and standard-series methods with mean errors as low as 2·5%.

C. D. KOPKIN

3694. **Determination of selenium and tellurium in bronze and copper.** V. I. Murashova and L. P. Bol'shakova. *Trudy Ural'sk. Politekh. Inst.*, 1960, (94), 158–160; *Ref. Zhur., Khim.*, 1960, (21), Abstr. No. 84,489.—Titrimetric methods are proposed for the determination of small amounts (0·048 to 0·098%) of Se and Te in bronze and copper. *Procedure for Se*—Dissolve 1 g of sample by heating with conc. HNO_3, add 1 g of $Pb(NO_3)_2$, and treat with an excess of aq. NH_3; Cu dissolves and Se and Te co-precipitate with $Pb(OH)_2$. Filter off the ppt., wash it with hot water, and dissolve it on the filter with a hot mixture of HCl and NaCl [1 litre of satd. NaCl soln. and 300 ml of HCl (1:1)]. Heat the soln. to dissolve the $PbCl_2$ and precipitate Se by heating for 15 min. with a 10% $SnCl_2$ soln. Filter off the ppt., wash it with hot HCl (1:20), transfer the filter to the pptn. flask, treat with 10 ml of conc. HCl and 5 or 6 drops of HNO_3, dilute to 150 ml, add 5 g of urea and boil. To the cooled soln. add excess of 0·03N-$Na_2S_2O_3$ and back-titrate with iodine soln., with starch as indicator. *Procedure for Te*—Carry out the preliminary procedure as described above, then to the soln. to be titrated add 10 ml of 30% KI soln. and titrate the resulting complex with 0·03N-$Na_2S_2O_3$. The error of the determinations is 0·03% (abs.) for Se and 0·001% (abs.) for Te.

C. D. KOPKIN

3695. **Spectrographic analysis of tellurium.** V. V. Polyakova and V. V. Fedorova. *Spektr. Anal. v Tsvet. Metall. M., Metallurgizdat*, 1960, 172–175; *Ref. Zhur., Khim.*, 1961, (3), Abstr. No. 3D153.—Silver, Cu, Bi, Sb, Pb, Mg, As, Au, Si, Al and Fe in the range 10^{-4} to 10^{-1}% are determined by an a.c. arc technique with a mean error of 10 to 20%.

K. R. COOK

3696. **Influence of iron on the colorimetric determination of chromium.** R. K. Korabel'nik. *Izv. Vyssh. Ucheb. Zavedenii, Khim. i Khim. Tekhnol.*, 1960, **3** (1), 189–192; *Ref. Zhur., Khim.*, 1960, (20), Abstr. No. 80,789.—The influence of Fe^{3+} on the photometric determination of Cr with diphenylcarbazide (**I**) is studied. The presence of large amounts of Fe^{3+} destroys the linearity of the calibration curve; H_3PO_4 slightly reduces the influence of Fe^{3+}, but decreases the intensity of the colour and increases the dispersion of the points on the curve. Potentiometric titration with $(NH_4)_2SO_4.FeSO_4.6H_2O$ soln. of a mixture of $Cr_2O_7^{2-}$ and Fe^{3+} has shown that Fe^{3+} cause an intermediate break in the potential curve, a shift of the end-point, and a decrease in the potential jump at the end-point. In the presence of H_3PO_4 the potentiometric titration curve is slightly more regular, but the end-point is still displaced. On titrating a mixture of $Cr_2O_7^{2-}$ and H_3PO_4 with $(NH_4)_2SO_4.FeSO_4.6H_2O$ soln. the end-point is displaced and the potential jump is decreased. The experiments are poorly reproducible and depend on the temp., which

explains the slow (≃50 min.) establishment of the equilibrium potential. Light has a strong influence on the reaction between $Cr_2O_7^{2-}$ and $(NH_4)_2SO_4$.$FeSO_4.6H_2O$, which takes place only in bright light. The reduced reproducibility of the determination of Cr in the presence of Fe^{3+} and H_3PO_4 is due to a change in the rate of oxidation of **I** by $Cr_2O_7^{2-}$, and to the reaction of **I** with the Fe^{3+} - H_3PO_4 complex (increasing the extinction).

C. D. KOPKIN

3697. **Spectrophotometric determination of chromium in uranium with 8-hydroxyquinaldine.** Kenji Motojima and Hiroshi Hashitani (Atomic Energy Res. Inst., Ibaraki-ken, Japan). *Anal. Chem.*, 1961, **33** (2), 239–242.—From 3 to 100 μg of Cr^{3+} in 50 ml of an acid soln. of the sample can be determined by extraction, with $CHCl_3$ at pH 5·3 to 6, of the Cr - 8-hydroxyquinaldine complex (after heating this at 60° to 70° for ≃ 8 min. and then cooling), and measuring the extinctions of the extract at 410 mμ and 580 mμ against a blank as reference (*cf. Japan Analyst*, 1960, **9**, 151). Uranium (⩾ 2·5 g is permissible) must be selectively masked with acetic acid, whilst Fe, Cu, Ni, Mo, V and Ti must be removed by washing the extract with a soln. containing 2M-ammonium carbonate, M-KCN and M-hydroxyammonium sulphate. The extinction at 580 mμ provides for a correction to be made for the small amount of residual Fe complex. Relatively high concn. of Cl^-, NO_3^- and SO_4^{2-} do not interfere. The standard deviation is 1·1% (several analyses), and the lower limit of determination is 1 p.p.m. of Cr.

W. J. BAKER

3698. **Gravimetric determination of molybdenum and its separation from other metals with *N*-benzoyl-*N*-phenylhydroxylamine.** S. K. Sinha and S. C. Shome (Presidency College, Calcutta, India). *Anal. Chim. Acta*, 1961, **24** (1), 33–36 (in English).—Sexavalent Mo is pptd. at 60° from an acid soln. by ethanolic *N*-benzoyl-*N*-phenylhydroxylamine. The ppt. may be weighed directly or ignited at 500° to 525° and weighed as MoO_3. In either case the accuracy is ≃ ±0·5%. The determination may be carried out in the presence of Cr^{VI}, Co^{II}, Ni^{II}, Cu^{II}, Fe^{III} and V^V.

A. C. R. HARTLEY

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C. D. KOPKIN

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K. R. COOK

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P. PEDERSEN

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III. Use of a multiple hollow-cathode source assembly and a 22-ft. direct-reading Eagle spectrograph. T. Lee and S. A. MacIntyre. *Ibid.*, 1961, **15** (2), 34–39.—Limitations of earlier procedures (Lee *et al.*, *Ibid.*, 1960, **14**, 39; Lee and Rogers, *Anal. Abstr.*, 1961, **8**, 3706, Part II) have been overcome with a 22-ft. spectrograph, using 5 in. of a concave grating (15,000 lines per in.) in the second order to provide a resolution of 15×10^4 and an inverse linear dispersion of 1·33 A per mm. Samples are excited by radiation from four hollow-cathode discharge lamps and an adjustable selector mirror. A complete analysis in duplicate (including a close comparison of unknown and standard) can be made in < 20 min., with a minimum error from exit-slit misalignment and a minimum loss of time caused by the pre-burn period. The results obtained by this method for concn. of ^{235}U from 10 to 85% agree closely with those obtained by the mass spectrometer, whilst the error over the range of 30 to 40% of ^{235}U is ± 0·17% (65 samples). A weak U line at 42440·9 A still interferes with the measurements, especially at low concn. of ^{235}U; corrections for the effect of concn. of ^{234}U and ^{236}U are generally necessary.

P. T. BEALE
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explains the slow (≃50 min.) establishment of the equilibrium potential. Light has a strong influence on the reaction between $Cr_2O_7^{2-}$ and $(NH_4)_2SO_4.FeSO_4.6H_2O$, which takes place only in bright light. The reduced reproducibility of the determination of Cr in the presence of Fe^{3+} and H_3PO_4 is due to a change in the rate of oxidation of **I** by $Cr_2O_7^{2-}$, and to the reaction of **I** with the Fe^{3+} - H_3PO_4 complex (increasing the extinction).

C. D. KOPKIN

3697. **Spectrophotometric determination of chromium in uranium with 8-hydroxyquinaldine.** Kenji Motojima and Hiroshi Hashitani (Atomic Energy Res. Inst., Ibaraki-ken, Japan). *Anal. Chem.*, 1961, **33** (2), 239–242.—From 3 to 100 μg of Cr^{3+} in 50 ml of an acid soln. of the sample can be determined by extraction, with $CHCl_3$ at pH 5·3 to 6, of the Cr - 8-hydroxyquinaldine complex (after heating this at 60° to 70° for ≃ 8 min. and then cooling), and measuring the extinctions of the extract at 410 mμ and 580 mμ against a blank as reference (*cf. Japan Analyst*, 1960, **9**, 151). Uranium (≯ 2·5 g is permissible) must be selectively masked with acetic acid, whilst Fe, Cu, Ni, Mo, V and Ti must be removed by washing the extract with a soln. containing 2M-ammonium carbonate, M-KCN and M-hydroxyammonium sulphate. The extinction at 580 mμ provides for a correction to be made for the small amount of residual Fe complex. Relatively high concn. of Cl^-, NO_3^- and SO_4^{2-} do not interfere. The standard deviation is 1·1% (several analyses), and the lower limit of determination is 1 p.p.m. of Cr.

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3710. **Radiochemical determination of radium in uranium milling process samples.** H. G. Petrow and R. Lindstrom (Ionics, Inc., Cambridge, Mass., U.S.A.). *Anal. Chem.*, 1961, **33** (2), 313–314.—A recent method (Petrow *et al.*, *Ibid.*, 1960, **32**, 926) is modified to increase the sensitivity and accuracy and shorten analysis time. The amount of inert material accompanying the Ra is decreased by substituting ammonium carbonate for Na_2CO_3 as the reagent for the conversion of $PbSO_4$ into Pb_3CO_3, and solvent extraction replaces the ion-exchange

step, Aliquat 336, a quaternary amine, being used as the extractant. The method is sensitive to 2 disintegrations per min. of Ra per litre provided that a 500-ml sample is taken. C. B. BAINES

3711. **Organic co-precipitants. XIII. Co-precipitation of quadrivalent plutonium.** V. I. Kuznetsov and T. G. Akimova. *Radiokhimiya*, 1960, **2** (3), 357–363; *Ref. Zhur., Khim.*, 1960, (21), Abstr. No. 84,437.—A method is developed for the pptn. of Pu from dil. soln., with separation from large amounts of other elements (other than U^{4+}, Th and Ce^{4+}), by co-pptn. (as a salt of $Pu(NO_3)_6^{2-}$) with a ppt. of the nitrate of rhodamine B butyl ester (butylrhodamine). To 200 ml of test soln. (containing > 0·01 μg of Pu and < 500 mg of other elements) add NH_4NO_3 to a concn. of 50% and HNO_3 to a concn. of 1·8N, then slowly add 1 g of phenolphthalein and 40 ml of 1% **I** soln. Set aside for 1 hr., filter, wash the ppt. (× 2) with a soln. 50% in NH_4NO_3 and 1·8N in HNO_3 to which sufficient butylrhodamine has been added to give a slight ppt., transfer the ppt. and filter to a porcelain crucible, add 2 ml of conc. $(NH_4)_2SO_4$ soln. and ignite at 550° to 600°. Determine the Pu content radiometrically. Double pptn. is required for the separation of Pu from large amounts of U^{VI} (Pu:U = 1:10). C. D. KOPKIN

3712. **Mercurimetric determination of chloride ion with a new indicator.** A. I. Zinov'ev and N. S. Solov'eva. *Trudy Vses. Nauch.-Issled. Geol.-Razved. Inst.*, 1960, (155), 325–328; *Ref. Zhur., Khim.*, 1960, (22), Abstr. No. 88,335.—The titration of Cl^- is carried out with $Hg(NO_3)_2$ soln., with a mixed indicator, diphenylcarbazone-bromophenol blue. If a yellow colour is obtained on adding the indicator to the test soln. add 0·05N-NaOH dropwise from a burette until a lilac colour appears, then neutralise with 0·05N-HNO_3 until the addition of one drop produces a yellow colour. If a lilac colour is obtained on addition of the indicator, neutralise with 0·05N-HNO_3. Titrate the soln. with 0·1N-$Hg(NO_3)_2$ to a lilac colour. The method is useful in the analysis of natural water. The accuracy compares favourably with that of the argentimetric method. K. R. COOK

3713. **An interpretation of the end-point error in the potentiometric titration of bromide and chloride mixtures with silver nitrate.** R. C. Bowers, L. Hsu and J. A. Goldman (Dept. of Chem., Northwestern Univ., Evanston, Ill., U.S.A.). *Anal. Chem.*, 1961, **33** (2), 190–194.—The bromide end-point error in the titration of mixtures of Br^- and Cl^- with $AgNO_3$ soln. can be minimised (1·2 to 1·5%, with equimolar concn. of Br^- and Cl^-) by adding sufficient electrolyte, *viz.* 80 mM-KNO_3 or 2·6 mM-$Ca(NO_3)_2$, to flocculate the AgBr as it forms. The extent of the error depends on the rate of addition of $AgNO_3$ soln. and the original ratio of Cl^- to Br^-. Any Cl^- in excess of that for ideal uniform mixed-crystal formation enters the AgBr and exchanges with Br^- in soln., only slowly during non-flocculating conditions, but very rapidly after flocculation. The distribution of Cl^- and Br^- between solid and soln. then approaches that required for ideal homogeneous mixed crystals. The error can be determined semi-quant. by assuming that the ratio of Cl^- to Br^- adsorbed on colloidal AgBr is proportional to the relative concn. of these ions in soln. and governs the relative amounts of these ions pptd. at any stage of the titration. These conclusions do not necessarily invalidate the findings of Kolthoff *et al.* (*J. Amer. Chem. Soc.*, 1939, **61**, 1036; 1954, **76**, 1503). W. J. BAKER

3714. **Precision null-point potentiometry. Direct micro-determination of iodide in solutions with high chloride concentrations.** H. V. Malmstadt and J. D. Winefordner (Dept. of Chem. and Chem. Engng, Univ. of Illinois, Urbana, U.S.A.). *Anal. Chim. Acta*, 1961, **24** (1), 91–96 (in English).—Micro amounts of iodide may be rapidly and accurately determined by this technique in the presence of a 2×10^6 excess of chloride. Brine and iodised-salt soln. containing respectively from 10 and 5 μg of iodide per ml were determined with an accuracy of ≃5%. A. C. R. HARTLEY

3715. **Polarographic determination of iodine in tellurium metal.** V. T. Athavale, R. G. Dhaneshwar, S. V. Gulavane and M. S. Varde (Anal. Div., Atomic Energy Estab. Trombay, Bombay, India). *Anal. Chem.*, 1961, **33** (2), 311–312.—The procedure described follows closely that developed by Miles *et al.* (A.E.R.E., Report I/R 1038, 1952), except that the final measurement is made polarographically instead of spectrophotometrically. The sample is oxidised with $K_2Cr_2O_7$ plus H_2SO_4 at 80°, oxalic acid is added, and the iodine is removed by distillation, absorbed in aq. NaOH, extracted into CCl_4, back-extracted into NaOH, and finally oxidised with Br in the presence of H_2SO_4. After the soln. has been concentrated by evaporation, the IO_3^- are determined polarographically at 30° with M-KCl and 0·05 M-$Na_2B_4O_7$ as supporting electrolyte. The $E_{\frac{1}{2}} = -1{\cdot}2$ V *vs.* the S.C.E. The recovery of iodine (1 to 10 μg) is >96%. W. J. BAKER

3716. **Photometric determination of iodates.** S. S. Vil'borg and V. A. Drozdov. *Izv. Vyssh. Ucheb. Zavedenii, Khim. i Khim. Tekhnol.*, 1960, **3** (1), 75–77; *Ref. Zhur., Khim.*, 1960, (20), Abstr. No. 80,838.—The method consists in photometry of the soln. of ellagic acid formed when tannin (**I**) reacts with IO_3^- in acid medium. The max. colour intensity is at pH 2·56; the colour develops within 3 min. and does not change for 1·5 hr. To construct a calibration curve, to 15 ml of a 3% **I** soln. add standard iodate soln. (0·094 to 1·452 mg of IO_3^-) and 4 ml of 2N-acetic acid, make up to 50 ml, and after 3 min. measure the extinction in a 20-mm cell with a blue filter. The blank contains all these components except the oxidant. Beer's law is obeyed. C. D. KOPKIN

3717. **A special adaptation of the Volhard method for the analysis of manganese oxide ores.** V. L. Garik and L. M. Silber (Microwave Res. Inst., Polytech. Inst., Brooklyn, N.Y., U.S.A.). *Anal. Chem.*, 1961, **33** (2), 319–320.—A rapid modified Volhard method for determining Mn^{3+} and Mn^{4+} in, *e.g.*, impure oxides ($xMnO.yMnO_2$), is based on extraction of Mn^{3+} with warm dil. H_2SO_4 and concurrent disproportionation of Mn^{3+} into Mn^{2+} and Mn^{4+}. The content of Mn^{II} is determined by first adjusting an aliquot of the warm soln. to pH 7·5 to 8·0 with 4N-Na_2CO_3 and then titrating with MnO_4^- reagent to the nearest 0·5 ml (addition of the alkali advances the apparent end-point 2 to 3%, thus making it more readily seen); this vol. of titrant is then added to another aliquot, the soln. is adjusted to pH 7 ± 0·2 with HCl, and the titration is completed at 85° to 95° to the usual end-point. The concn. of MnO_2 (unaffected by the analytical

procedure) can be calculated from the total content of Mn (determined by a separate Volhard titration in the presence of low concn. of Cl^-) and from the Mn assigned to MnO. The precision of the method is 0·2 to 0·3% and the absolute accuracy is ±0·25% (based on blank runs). W. J. BAKER

3718. **Spectrophotometric determination of rhenium with 4-methylnioxime.** J. L. Kassner, Shih-Fan Ting and E. L. Grove (Sch. of Chem., Univ. of Alabama, University, U.S.A.). *Talanta*, 1961, **7** (3–4), 269–275 (in English).—Rhenium forms a stable chelate with 4-methylnioxime (4-methylcyclohexane-1,2-dione dioxime) (**I**). Interfering ions present in molybdenite concentrates are first removed by evaporation with HCl, pptn. of hydroxides with aq. NH_3 soln. and $CHCl_3$ extraction of ethyl xanthate complexes. *Procedure*—To 5 ml of soln. (pH ≃ 7) containing > 160 μg of perrhenate add 25 ml of saturated aq. **I** soln. and 5 ml of $SnCl_2$ soln. (3 g of $SnCl_2.2H_2O$ in 40 ml of conc. HCl, diluted to 100 ml) and dilute to 50 ml. After 5 min. extract with 4, 3 and 3 ml of $CHCl_3$ and adjust the vol. to 10 ml. Measure the extinction at 436 mμ. P. D. PARR-RICHARD

3719. **Spectrometric determination of rhenium in alloys.** I. P. Kharlamov, P. Ya. Yakovlev and M. I. Lȳkova (I. P. Bardin Central Sci. Res. Inst. of Ferrous Metall.). *Zavod. Lab.*, 1961, **27** (2), 141–143.—The sample (0·1 to 2 g, together with 0·1 g of Fe if the alloy is Ni-, Co- or Cr-based) is dissolved in a mixture of HCl and HNO_3 (3 : 1) (60 ml) and the soln. is evaporated twice to fuming with 10 ml of H_2SO_4. The residue is dissolved in 80 ml of water and the soln. is poured into 50 to 100 ml of boiling 25% NaOH soln. The soln. is diluted to 500 ml and filtered after 1 to 2 hr. An aliquot (250 ml) is adjusted to a pH of between 5·5 and 7·5 with H_2SO_4 (1 : 4) and diluted to 500 ml. The extinction of the perrhenate is measured at 224 mμ. G. S. SMITH

3720. **The use of X-ray fluorescence analysis in the iron-smelting industry.** H.-J. Kopineck and P. Schmitt (Res. Inst. Hoesch A.-G. Westfalenhütte, Dortmund). *Arch. Eisenhüttenw.*, 1961, **32** (1), 19–29.—Applications of this technique are surveyed, with special reference to the limits of detection, the analysis of metallurgical slags, especially Siemens-Martins slags, the mutual effect of two elements, and the determination of trace elements. Results indicate that the method is suitable for the analysis of ores, slags and refractories, but only in special cases for the analysis of steel. (22 references.) M. LAPIDOT

3721. **Potassium [ammonium] thiocyanate as an ndicator in the determination of iron with EDTA (disodium salt).** A. A. Bashkirtseva and E. M. Yakimets. *Trudȳ Ural'sk. Politekh. Inst.*, 1960, (94), 110–116; *Ref. Zhur., Khim.*, 1960, (21), Abstr. No. 84,462.—The reaction of EDTA (disodium salt) with Fe^{3+} in the presence of SCN^- is studied. The optimum conditions for the complexometric determination of Fe with SCN^- as indicator are—concn. of KSCN or NH_4SCN 0·3M, content of Fe 0·01 to 1 mg in 100 ml, pH 1·5 to 2, temp. 50° to 60°. The titration is carried out in the presence of an oxidant [$(NH_4)_2S_2O_8$ or H_2O_2] to avoid reduction of Fe^{3+} by the thiocyanate. For a content of Fe of 0·1 to 1 mg in 100 ml, direct titration, and for 0·01 to 0·1 mg of Fe in 100 ml, back-titration, is used. No interference is caused by the following (max. permissible amounts in mg per 100 ml in brackets)—Al^{3+} (5); Ca^{2+} (1000); Cu^{2+} (0·5); Cr^{3+} (20); Mg^{2+} (1000); Mn^{2+} (200); Na^+ (1000); K^+ (1000); Ni^{2+} (1); Zn^{2+} (15); Cl^- (1000); F^- (20); $H_2PO_4^-$ (100); NO_3^- (1000); SO_4^{2-} (50); and $Cr_2O_7^{2-}$ (2). The indicator is sensitive to 1×10^{-1} g of Fe per ml. The titration of Fe in organic solvents (ethyl ether and isoamyl alcohol and their mixtures, and mixtures of butyl acetate with isoamyl alcohol) was not satisfactory. C. D. KOPKIN

3722. **Sulphosalicylic acid as an indicator in the determination of iron with EDTA (disodium salt).** A. A. Bashkirtseva and E. M. Yakimets. *Trudȳ Ural'sk. Politekh. Inst.*, 1960, (94), 117–121; *Ref. Zhur., Khim.*, 1960, (21), Abstr. No. 84,463.—Conditions are found for the complexometric titration of Fe^{3+} in the presence of sulphosalicylic acid (**I**) as indicator. A study of the rate of reaction of EDTA (disodium salt) with Fe^{3+} in the presence of Na sulphosalicylate has shown that Fe (> 1 mg in 100 ml) can be titrated at pH 3 to 4 at room temp. or at pH 1 to 2 at 60° to 70°. The sensitivity of **I** at pH 1 is $6·0 \times 10^{-7}$ g of Fe per ml. No interference is caused by the presence of Co^{2+}, Mg^{2+}, Na^+, K^+, Cl^- or NO_3^-; at pH 1·5 the following (in mg) do not interfere: Al^{3+}, < 5; Cu^{2+}, < 0·5; Cr^{3+}, < 20; Fe^{2+}, < 14; Mn^{2+}, < 200; Ni^{2+}, < 1; Zn^{2+}, < 15; $H_2PO_4^-$, < 200; SO_4^{2-}, < 400; and $Cr_2O_7^{2-}$, < 2. With a ratio of F^- to Fe^{3+} > 3, F^- are complexed with Al. To determine Fe in materials free from interfering elements (*e.g.*, carbon ash, chamotte, dolomite, bauxite and slimes from aluminium production), heat an aliquot of the soln. to boiling after removal of H_2SiO_3, add an oxidant ($S_2O_8^{2-}$, H_2O_2 or HNO_3), boil for 1 or 2 min., neutralise with 2N-alkali to a turbidity, add 10 ml of N-HCl and 1 ml of **I** or Na sulphosalicylate soln., dilute to 100 ml and titrate with a soln. of EDTA (disodium salt) till the lilac colour is discharged. C. D. KOPKIN

3723. **Bromatometric determination of ferrous ions. Determination of ferrous oxalate with bromine chloride.** J. Laszlovszky (Inst. f. anorg. u. anal. Chem., L. Eötvös Univ., Budapest, Hungary). *Pharm. Zentralh.*, 1961, **100** (2), 77–80.—*Procedure*—Dissolve the sample (≃ 1 milli-equiv.) in warm 20% HCl (15 ml) in the presence of a little pentane to exclude atmospheric O, add conc. H_3PO_4 soln. (10 ml), H_2O (6 to 8 ml) and $HgCl_2$ (1 to 1·5 g), mix until dissolved and titrate at 30° to 35° with 0·1N-BrCl or 0·1N-$KBrO_3$, with *p*-ethoxychrysoidine as indicator. The results of 12 assays of a sample of $(NH_4)_2SO_4.FeSO_4.6H_2O$ ranged from 99·23% to 100·18%; the results of 9 assays of a sample of ferrous oxalate ranged from 98·84% to 99·96%. A. R. ROGERS

3724. **Contributions to the complexometric determination of cation mixtures. III. Simultaneous titration of iron(III) and aluminium in the presence of ammonium thiocyanate as indicator.** C. Liteanu, I. Lukács and C. Strusievici (Romanian Acad. Sci., Cluj). *Anal. Chim. Acta*, 1961, **24** (2), 200–202 (in English).—The method is based on the slow rates of formation and decomposition of the Al - EDTA complex. The soln. for analysis should contain 0·5 to 6 mg of Fe^{3+} and 1 to 30 mg of Al^{3+} in 10 ml, but the ratio of Fe^{3+} to Al^{3+} must be > 1 : 4. The pH should be ≃ 2. *Procedure*—To the soln. (10 ml) add 5 drops of 1% aq. NH_4SCN soln. and titrate the Fe^{3+} with 0·05M-EDTA (disodium salt). The end-point is marked by a change from red to yellow.

Then add a known vol. of 0·05M-EDTA, <3 ml in excess of that required to complex the Al^{3+}. Add 1 g of ammonium acetate, adjust the pH to between 5 and 7 with conc. aq. NaOH soln. and add 1 ml of satd. aq. NH_4SCN soln. and sufficient acetone to produce a final concn. of 50% at the end-point. Titrate the excess of EDTA with 0·05M-$Co(NO_3)_2$. The colour change at the end-point is from pink - orange to blue - green; in the absence of Fe the change is from pink to greyish-blue. H. N. S.

3725. **Separation of vanadium and chromium from iron by extraction of ferric chloride with isopropyl ether.** G. A. Dean and J. F. Herringshaw (Chem. Dept., Imperial Coll. of Sci. and Technol., London). *Analyst*, 1961, **86**, 106–110.—The method proposed was carried out on a mixture of $FeCl_3$.-$6H_2O$, CrO_3 and V^V (in chloride soln.). The sample is evaporated with HCl only until a scum just forms, and the cooled residue is dissolved in HCl (10 to 11M) saturated with SO_2. After 5 min. the liquid is shaken with an equal vol. of isopropyl ether. The separated organic layer is washed two or three times with half its vol. of 8M to 9M-HCl and these washings are added to the main aq. layer. By this method 99·95% of the Fe present is extracted in the organic layer with negligible extraction of V and Cr. A. O. Jones

3726. **Microcrystalloscopic detection of ferricyanide ions with 4-hydroxyquinaldine ethochloride.** A. S. Babenko and Z. Ya. Kralner. *Izv. Výssh. Ucheb. Zavedenií, Khim. i Khim. Tekhnol.*, 1960, **3** (1), 62–65; *Ref. Zhur., Khim.*, 1960, (20), Abstr. No. 80,731.—4-Hydroxyquinaldine ethochloride forms a yellow - green ppt. with $Fe(CN_6)^{3-}$, consisting of tetragonal crystals, often in rosettes. With I^-, SCN^- and ClO_4^-, colourless crystals are obtained, in clusters of straight needles and multi-rayed stars collected in thick rosettes; the same type of crystal is given by $Cr_2O_7^{2-}$ (bright yellow) and MnO_4^- (violet). C. D. Kopkin

3727. **Ion-exchange resins in steel analysis.** F. M. Hall and A. Bryson (Univ. of New South Wales, Wollongong Div., Australia). *Anal. Chim. Acta*, 1961, **24** (2), 138–142 (in English).—Vanadium, Cr and Mo are separated from other constituents of steel by passing an acetate-buffered soln. of the sample, containing mannitol, through a column of a strongly basic ion-exchange resin. The three metals are retained on the resin and are subsequently eluted selectively. *Procedure*—Dissolve 0·5 g of the steel in 20 ml of 4N-H_2SO_4 and digest for <1 hr. with a few drops of conc. HNO_3. Filter off WO_3 and other insoluble substances, add to the filtrate 5 ml of N-$AgNO_3$, a few drops of 5% $KMnO_4$ soln. and 2 g of $(NH_4)_2S_2O_8$, and boil. Add 15 ml of N-NaCl and boil to destroy MnO_4^-. Cool, filter, add 1 g of mannitol and 2 g of ammonium acetate, dilute to $\simeq$200 ml and add aq. NH_3 to adjust the pH to 2·3 to 3. Pass the soln. through 25 ml of De-Acidite FF resin (nitrate form) at a rate of 15 drops per min. and wash the resin with $\simeq$100 ml of water. Elute the V with 200 ml of 0·6N-NaOH (5 to 10 drops per min.) and wash the column with water to give a total eluate of 250 ml. Elute the Cr with 200 ml of 8N-HCl and the Mo with 200 ml of N-HCl. The three metals are then determined by standard procedures. H. N. S.

3728. **Application of gas chromatography to the determination of hydrogen, nitrogen and oxygen in steel and cast iron.** P. Tyou and A. Hans (Centre Nat. de Rech. Métall., Liége, Belgium). *Rev. Métall.*, 1961, **58** (2), 187–193.—The principles of gas chromatography are discussed. It is shown that it is possible to improve sensitivity to CO and N by placing the katharometer block and the column in separate thermostats. It is then possible to obtain sharper and better separated peaks while maintaining the maximum sensitivity of the katharometer. The best results were obtained with a molecular sieve column (2 metres $\times$ 0·25 in.) at 40° to 60° and the katharometer at 0°, with an Ar flow-rate of 2 litres per hr. A. J. Bennett

3729. **Determination of oxygen and hydrogen in steel by carrier gas techniques.** C. E. A. Shanahan. *Rev. Métall.*, 1961, **58** (1), 55–64.—*Determination of O*—The sample (5 to 10 g) is heated to 1750° in a carbon crucible in a current of Ar. The CO formed is oxidised to CO_2 by passage through a mixture of CuO and Fe_2O_3 at 550°. The gas mixture is then washed with chromic - sulphuric acid and passed through a sintered glass filter, and the CO_2 is absorbed by soda-asbestos. The time required is 15 min. The standard deviation on samples containing 0·034% of O was $\pm$ 0·0016% (30 determinations). *Determination of H*—The sample (50 g) is heated at 650° for 30 min., and the H liberated by diffusion is carried by a current of dry H through a Fe_2O_3 - CuO mixture at 550° to 600°. The H_2O formed is determined by absorption in methanol and titration with Karl Fischer reagent. A. J. Bennett

3730. **Nitrogen determination in steel, cast iron and ferro-alloys.** J. Calmettes and H. Guinot. *Rev. Métall.*, 1960, **57** (10), 925–933.—When total N is determined by wet methods the results of titrimetric determinations are higher than the results of colorimetric determinations. This difference is influenced by the type of apparatus used, and is increased after recarburisation and after calcium silicide additions, and may be due to the presence in the sample of complex N-containing phases. Nitrogen can be determined by measurement of the N liberated on fusion of the sample (1 g) with basic lead chromate (5 g), which is obtained by fusing $PbCrO_4$ (50 g) with NaOH (8 g) at 900°. It is suggested that N in the form of Si_3N_4 may be determined from the difference between the results obtained by oxidative fusion at 840° and 930°. This difference is insignificant for arc-furnace steels containing $>0·3$% of Si, but is significant for high-frequency-furnace steels containing $\simeq$2% of Si. A. J. Bennett

3731. **Evaluation of the formate method for the simultaneous polarographic determination of copper and lead in steel.** P. H. Scholes (B.I.S.R.A., Hoyle St., Sheffield, England). *Analyst*, 1961, **86**, 116–124.—The sample (1 g) is dissolved in 12 ml of HCl (1 : 1). With samples containing $>0·3$% of Cu, with or without Pb, a smaller wt. is taken and the 1 g is made up with pure iron. The soln. is oxidised with $KClO_3$ soln. and the liquid is concentrated to 6 or 7 ml by gentle boiling. To the soln., removed from the source of heat, are added 5 ml of 20% hydrazine hydrochloride soln., 5 ml of satd. Na formate soln. and 2 ml of starch soln., and the liquid is maintained at $\simeq$90° for 10 min. after the apparently complete reduction of Fe. The cooled soln. is diluted to 20 ml, 2 to 3 ml is de-oxygenated with N in the cell of a cathode-ray polarograph, and the peak heights of the waves for Cu and Pb are measured and referred to calibration graphs, which

are prepared with Cu-free or Pb-free iron soln. to which, after oxidation, standard Cu or Pb soln. is added. Bismuth (Bi:Cu = 2:1) does not interfere. With samples containing 0·2 to 2·0% of Mo a smaller wt. is diluted to 1 g with pure iron so that the Mo content does not exceed 2 mg. A method is also described in which Cu can be determined down to a lower limit of 0·0001% after removal of Fe by extraction with isobutyl acetate.

A. O. JONES

3732. **Spark spectrographic procedure for the determination of boron in sheet steel.** E. F. Runge and F. R. Bryan (Ford Motor Co., Dearborn, Mich., U.S.A.). *Appl. Spectroscopy*, 1961, **15** (1), 13–15.—Improved line-to-background ratio for B 2496·78 A is obtained by rotating the sample at 1 r.p.m. so that new sample surface over a circle of 1·6 cm diam. is continually presented to the graphite counter-electrode. A spark source with 200 μH added inductance also enhances the line-to-background ratio. The sample is supported horizontally on a massive brass platform, with a powdered copper bed to ensure good thermal and electrical contact with the 0·05-in.-thick specimen and so avoid over-heating. Repeat sparkings on 10 separate samples cut from the same sheet gave a coeff. of variation of 3·17% at the level of 0·004% of B.

P. T. BEALE

3733. **Determination of cerium in medium- and high-alloy steel.** A. A. Fedorov and F. A. Ozerskaya (I. P. Bardin Central Sci. Res. Inst. of Ferrous Metall.). *Zavod. Lab.*, 1961, **27** (2), 139–140.—The sample (1 g) is heated with 30 to 40 ml of 40% HF and 2 to 3 ml of 30% H_2O_2 soln. The treatment is repeated until the sample is dissolved. After addition of 30 ml of a soln. of 1 g of CaO in 1 litre of water the soln. is evaporated to dryness. The residue is treated with 30 to 40 ml of water and 15 to 20 ml of 40% HF and the soln. is evaporated to dryness. This treatment is repeated. The residue is heated with 30 to 40 ml of water, 10 to 15 ml of 40% HF is added, and the soln. is heated for 15 to 20 min. to coagulate the CaF_2, which is used as a collector of the Ce. The ppt. is filtered off, washed with 2% HF and then washed into the platinum dish used for dissolution. The filter is ashed and the residue is added to the soln., which is then evaporated to dryness. The residue is repeatedly evaporated with conc. HNO_3 (5 to 6-ml portions) until HF is removed. The residue is dissolved in 10 to 15 ml of conc. HNO_3 and the soln. in a beaker is evaporated to dryness. Several evaporations with conc. HCl are carried out to remove NO_3^- and the residue is finally dissolved in 3 to 5 ml of conc. HCl and evaporated almost to dryness. Saturated oxalic acid soln. (15 ml) is added, followed, after the formation of a ppt., by 10 ml of water. The soln. is boiled for 1 to 2 min. and set aside for 12 hr. The ppt. is collected and washed with cold 1% oxalic acid soln. The filter and ppt. are boiled for 2 to 3 min. with 10 ml of a soln. prepared by dissolving 10 g of boric acid and 200 g of K citrate in 100 ml of water and filtering, and 15 to 20 ml of water. The filtered soln. is evaporated to a vol. of 20 to 25 ml and cooled. It is then treated with 20 drops of 1% NaOH soln., 5 drops of 10% H_2O_2 soln. and 15 drops of 25% aq. NH_3. After 15 min. the soln. is diluted to 50 ml, and the extinction of the yellow complex formed with K citrate in the presence of H_2O_2 is measured.

G. S. SMITH

3734. **Polarographic determination of tin in stainless steel.** K. R. J. Cottell [U.K.A.E.A. (Res. Group), Chem. Div., Chatham Outstation, Riverside, Kent]. Analytical Method AERE–AM77, 1961. 4 pp.—This method, based on that of Allsopp and Damerall (*Anal. Chem.*, 1949, **21**, 677), is suitable for use with a cathode-ray polarograph. Upwards of 10 μg of Sn can be determined with an error $\gtrsim \pm 5\%$.

J. W. PRICE

3735. **Spectrophotometric determination of titanium in steel.** J. Korkisch (Anal. Inst., Univ., Wien, Austria). *Mikrochim. Acta*, 1961, (2), 262–267 (in German).—Titanium is separated from V, Mo, Zr and other elements that interfere with its spectrophotometric determination with ascorbic acid by adsorption of the fluoride complex on strongly basic anion-exchange resin and elution with 0·1N-H_2SO_4 containing H_2O_2. *Procedure*—Prepare a sample soln. containing $\gtrsim 500$ μg of Ti in 0·1N-H_2SO_4 (100 ml) and free from Cl^- and NO_3^-. Add 10% NaF soln. (10 ml) and pass the soln. through a column of Dowex 1-X8 anionic resin (SO_4^{2-} form). Wash the resin first the 0·1N-H_2SO_4 (100 ml) containing 10% NaF soln. (10 ml) and then with 0·1N-H_2SO_4 (30 ml). Elute the Ti with (0·1N-H_2SO_4 (50 ml) containing 30% H_2O_2 soln. (5 ml). Evaporate the eluate to dryness and ignite the residue to red heat. Add a small amount of conc. HF and evaporate to dryness on a water bath. Dissolve the residue in N-HCl (20 ml), add $AlCl_3$ soln. (40 g of $AlCl_3.6H_2O$ in 100 ml of N-HCl) (5 ml) and 2·5M-Na acetate (12·5 ml) and dilute to 50 ml with 5% ascorbic acid soln. buffered to pH 3·8 with Na acetate. Measure the extinction at 355 mμ. Recoveries of 200 μg of Ti added to 5 different alloys ranged from 195 to 210 μg.

W. T. CARTER

3736. **Co-precipitation of phosphate with lead molybdate in the British Standard method for determining phosphorus in steel.** R. B. Heslop and R. Kirby (Chem. Dept., Coll. of Sci. and Technol., Sackville St., Manchester, England). *Analyst*, 1961, **86**, 134–135.—The soln. of steel (2 g) in HNO_3 and HCl was evaporated to fuming with $HClO_4$, the residue was boiled with HCl and water, and any insol. residue was filtered off and re-treated similarly. The combined filtrates were evaporated to fuming with HBr, the residue was dissolved in water, NH_4NO_3 was added with $\simeq 2$ μC of ^{32}P (as PO_4^{3-}), and the P was pptd. at 80° as ammonium molybdophosphate. The collected washed ppt. was dissolved in 50% aq. NH_3, and Mo was re-pptd. as lead molybdate with Pb acetate. The filtrate from the washed ppt. was diluted to 500 ml and a 10-ml aliquot was counted. The ppt. was dissolved in dil. NaOH soln. and the soln., diluted to 10 ml, was counted. The amount of total PO_4^{3-} carried down with the ppt. was calculated from the corrected counts. A tendency appeared towards greater pptn. of PO_4^{3-} as the P content of the steel increased, but the highest value recorded in a single experiment corresponded to an increase of only 0·32% of the wt. of the lead molybdate. Stockdale (*Ibid.*, 1958, **83**, 24) reported that co-pptn. of PO_4^{3-} caused final results to be high by $\simeq 1$ in 200. The determination now described indicates that, with steels of medium P content, Stockdale's estimate is high by a factor of about 3.

A. O. JONES

3737. **Analytical chemistry of alloying elements [in steel]. I. Colorimetric methods of determination of niobium.** I. S. Mustafin and L. A. Molot.

Uch. Zap. Saratovsk. Univ., 1959, **71**, 177–181; *Ref. Zhur., Khim.*, 1960, (21), Abstr. No. 84,453.—The photometric method described is based on the formation at pH 4·3 of an orange compound of Nb with alizarin (**I**) with a ratio of Nb to **I** of 1:3. Beer's law is obeyed at concn. of Nb from 5 to 30 μg per ml. *Procedure*—Heat 0·4 g of sample with 20 ml of HCl (1:1), add 4 drops of conc. HNO_3, evaporate to 3 or 4 ml, add hot water to 200 ml and 1 g of Na_2SO_3, boil for 5 min., set aside for 20 min. in the dark and filter. Wash the ppt. twice with acidified water, and evaporate the filtrate and washings. Dry and ignite the ppt., then fuse it for 30 min. with 0·4 g of $K_2S_2O_7$ at 400° to 500°, and treat the melt with a soln. of 0·7 g of ammonium oxalate. Add the resulting soln. to the evaporated filtrate, dilute to 200 ml (in the presence of large amounts of Ni, filter off the pptd. Ni oxalate) add 0·1% **I** soln. and a soln. of EDTA (disodium salt) (2·5 g in 30 ml) and measure the extinction at pH 4·4. No interference is caused by the presence of a threefold excess of W, a twofold excess of Mo, a 20-fold excess of Ti, or large amounts of Ni and Cr. It is shown that the thiocyanate method for determining Nb in steel can be employed without preliminary separation of Nb as Nb_2O_5. The analysis then takes 90 min. C. D. KOPKIN

3738. **Colorimetric determination of molybdenum in steel with Acid Chrome blue 2K as reagent.** V. P. Kondratova and V. I. Petrashen'. *Trudy Novocherk. Politekh. Inst.*, 1959, **97**, 177–179; *Ref. Zhur., Khim.*, 1960, (20), Abstr. No. 80,795.—The colorimetric determination of Mo with Acid Chrome blue 2K (*Anal. Abstr.*, 1961, **8**, 3699) is used for determining Mo in steel not containing Cu or W, after preliminary removal of Fe^{3+} as the hydroxide. Dissolve 0·5 g of sample by heating with 10 ml of H_2SO_4 (1:4), add HNO_3 till foaming ceases, evaporate to 0·5 ml, add 10 ml of hot water, and precipitate Fe with conc. aq. NH_3. Filter off the ppt. and wash it (× 3) with hot water. Make the filtrate up to 50 or 100 ml, and use an aliquot for the colorimetric determination of Mo; the concn. in the final soln., of vol. 5 ml, should be 2 to 35 μg of Mo per ml. C. D. KOPKIN

3739. **The precipitation of hydrated cobalt 1-nitroso-2-naphthoxide from homogeneous solution.** A. H. A. Heyn and P. A. Brauner (Dept. of Chem., Boston Univ., Mass., U.S.A.). *Talanta*, 1961, **7** (3–4), 281–287 (in English).—Bivalent Co reacts with a mixture of HNO_2 and 2-naphthol (**I**) to give Co^{III}, which is pptd. as the 1-nitroso-2-naphthoxide. *Procedure*—To 10 ml of neutral soln. (1 to 90 mg of Co) add 10 drops of acetic acid, ice and 1 g of $NaNO_2$. After 10 min. add 25% NH_4F soln. (100 ml) to complex Fe and W, and an appropriate vol. of 0·5% **I** soln. in 25% acetic acid. Cool for 30 min. and decant the clear yellow liquid through an unweighed crucible. Wash the ppt. by decantation with (*i*) hot HCl (1:20), (*ii*) hot aq. NH_3 (1:10), and (*iii*) hot acetic acid (1:10). Finally wash the ppt. with hot HCl (1:10) until the washings are colourless; transfer the ppt. to the crucible, dry at 115° and weigh. Dissolve the ppt. in $CHCl_3$, dry and re-weigh. P. D. PARR-FICHARD

3740. **Accurate determination of cobalt. II. Gravimetric methods and in particular the phosphate method.** A. G. Foster and W. J. Williams (Royal Holloway College, Englefield Green, England). *Anal. Chim. Acta*, 1961, **24** (1), 20–32 (in English).—Determinations of Co by anthranilate and phosphate precipitations and electrolysis have been examined. The anthranilate and electrolysis methods give high results. The phosphate method [pptn. with $(NH_4)_2HPO_4$ and ignition of the ppt. to $Co_2P_2O_7$, and determination of residual Co in the filtrate spectrophotometrically, with nitroso-R salt, at 545 mμ] is recommended and has been developed to an accuracy of $\pm$0·2%. A. C. R. HARTLEY

3741. **Catalytic analysis. I. Determination of sub-micro amounts of cobalt by the tiron - hydrogen peroxide and the tiron - 2,7-dihydroxynaphthalene - hydrogen peroxide reactions.** J. Bognár and O. Jellinek (Tech. Univ., Miskolc, Hungary). *Magyar Kém. Foly.*, 1961, **67** (2), 73–78.—The catalytic effect of Co^{2+} on the oxidation of tiron by H_2O_2 in alkaline medium can be used for the determination of 10^{-4} μg of Co^{2+} in 5 ml of soln. Alternatively, the catalytic effect of Co^{2+} on the oxidation of tiron - 2,7-dihydroxynaphthalene by H_2O_2 in alcoholic medium may be employed; a minimum of 5×10^{-5} μg of Co^{2+} can then be determined in 5 ml of soln. The rate of each reaction is affected by pH, and is at a maximum at pH 10·6 and in the range 9 to 10·5, respectively. The dependence of reaction rate on temperature and H_2O_2 concn. is also discussed. The effects of the presence of Ag, Pb, Hg, Cu, Bi, Cd, As, Sb, Sn, Ni, Fe, Al, Cr, Zn, Mn, Ca, Sr, Ba, Mg, Na, K, Au, Pd, Pt, Mo, Se, Te, V, W, Ti, Tl, U, Zr, OsO_4 and NH_4^+ are tabulated; Ni^{2+} and OsO_4 interfere in both methods because of their catalytic action. B. VASZKO

3742. **Micro-determination of cobalt in reactor-grade zirconium.** J. Vogel, D. Monnier and W. Haerdi (Lab. de Chim. Minérale, Chim. Anal. et Microchim., Univ., Genève, Switzerland). *Anal. Chim. Acta*, 1961, **24** (1), 55–60 (in French).—The sample of zirconium is dissolved in HF - aqua regia (1:200), a soln. containing ^{60}Co as tracer is added, followed by a little $AlCl_3$ to complex F^-. The soln. is evaporated and the residue is dissolved in 9N-HCl and passed through a column of ion-exchange resin (Dowex 1-X8). Cobalt is retained as a complex anion, then eluted with 4N-HCl, extracted from the eluate as the dithizone complex, and finally determined spectrophotometrically at 520 mμ with nitroso-R salt. The method is sensitive to 0·0003% of Co with an accuracy of $\pm$4%. A. C. R. HARTLEY

3743. **Determination of radioactive cobalt in mixtures of radionuclides.** R. B. Hahn and D. L. Smith (Chem. Dept., Wayne State Univ., Detroit, Mich., U.S.A.). *Talanta*, 1961, **7** (3–4), 291–295 (in English).—The recovery of ^{60}Co by pptn. as the mercurithiocyanate and as the anthranilate was investigated; yields were 100·1 and 99·2%, respectively. The former precipitant was more selective for Co. Preliminary separation from fission products and from Ni is described. P. D. PARR-RICHARD

3744. **Separation of small amounts of cobalt from large amounts of nickel.** I. P. Alimarin and A. A. Bragina. *Trudy Komiss. Anal. Khim., Akad. Nauk SSSR*, 1960, **12**, 377–382; *Ref. Zhur., Khim.*, 1960, (23), Abstr. No. 92,006.—The co-pptn. of Co with MnO_2 is studied. At least 20 mg of MnO_2 is required for the complete co-pptn. of 5 to 750 μg of Co. To obtain a powdery easily centrifuged ppt., 1 to 2 g of phenylarsonic acid should be added. A method is developed for the determination of small

amounts of Co, based on its co-pptn. with MnO_2 and subsequent colorimetry with thiocyanate. The method can be used to determine Co (0·002%) in nickel metal and salts. C. D. KOPKIN

3745. **Respropiophenone oxime as a reagent for the determination of nickel.** J. S. Dave and A. R. Patel (Chem. Dept., M.S. Univ., Baroda, India). *J. Sci. Ind. Res., India, B*, 1961, **20** (2), 81.—The soln. of Ni in HCl is diluted to $\simeq$ 200 ml and heated to $\simeq$ 80°. A slight excess of reagent [1% soln. of respropiophenone (2,4-dihydroxypropiophenone) in ethanol] is added dropwise with constant stirring, followed by dil. aq. NH_3 until pptn. is complete. The mixture is digested on a boiling-water bath for $\simeq$ 1 hr., and the yellowish-green ppt. is then collected in a sintered-glass crucible, washed with hot water, dried at 110° to 120° and weighed as $Ni(C_9H_{10}NO_2)_2$. Amounts of Ni in the range 7 to 30 mg are determined with an accuracy of $\simeq \pm 0{\cdot}3\%$. J. H. WATON

3746. **Spectrographic analysis of high-purity nickel.** D. M. Shvarts and I. S. Nilova. *Trudy Komiss. Anal. Khim., Akad. Nauk SSSR*, 1960, **12**, 366–376; *Ref. Zhur., Khim.*, 1961, (3), Abstr. No. 3D159.—After dissolution of the sample in HNO_3, evaporation, and ignition to NiO, pellets are prepared and arced (the techniques are described in detail). The following elements are determined in the range 10^{-4} to 2×10^{-3} %, with a coeff. of variation of 5 to 15%—Bi, Sn, Zn, Sb, Pb, Cd, As, Fe, Si, Al, Mg, Cu, Co, Mn and Cd. K. R. COOK

3747. **Separation of platinum elements by ion exchange.** E. Blasius and D. Rexin (Anorg.-Chem. Inst. der Tech. Univ., Berlin). *Z. anal. Chem.*, 1961, **179** (2), 105–116 (in German).—A survey is given of the separation of Rh, Pd, Ir and Pt as chloro-, hydroxo- and nitrito-complexes on anion and cation exchangers. Procedures are proposed for the separation of binary and ternary mixtures. T. R. ANDREW

3748. **Photometric determination and separation of ruthenium by acetylacetone.** J. Brandštetr and J. Vřešťál (Inst. Gen. and Anal. Chem., Tech. Highschool, Brno, Czechoslovakia). *Coll. Czech. Chem. Commun.*, 1961, **26** (2), 392–397 (in German).—The red complex of Ru^{III} with acetylacetone (**I**), formed in warm soln., is useful for the photometric determination in $CHCl_3$ of Ru (0·4 to 20 μg per ml) and has max. absorption at 505 mμ (ϵ 1510). The colour intensity of the $CHCl_3$ soln. changes with pH and is maximum at pH 3·73. The **I** complexes of interfering ions (Fe^{3+}, Ti, V, Al) are removed by extraction with $CHCl_3$ from cold aq. soln. of pH 1·8 to 2. *Procedure*—Boil the soln. (15 to 25 ml) containing Ru (10 to 700 μg) under reflux with **I** (4 ml) and $CHCl_3$ (3 ml); when a pink colour appears add 2% $NaHCO_3$ soln. dropwise until the aq. layer is decolorised. Cool, separate, and extract the aq. phase with **I** - $CHCl_3$ (1:2) (3 × 5 ml). Dry the combined organic phases, dilute to 25 ml with **I** - $CHCl_3$, and compare the extinction at 505 mμ with a calibration curve. J. P. STERN

3749. **New fire-assay method for rhodium.** B. R. Sant and F. E. Beamish (Dept. of Chem., Univ., Toronto, Ont., Canada). *Anal. Chem.*, 1961, **33** (2), 304–305.—From 10 μg to 10 mg of Rh in a roasted sulphide concentrate ($\simeq$80 g, 45 mesh) can be collected in a Cu - Ni - Fe button (25 to 30 g) by the fire-assay method of Beamish *et al.* (*cf. Anal. Abstr.*, 1960, **7**, 1032). The button is dissolved in HCl and the base metals are removed by retention on a 70-cm column of cation-exchange resin (Dowex 50-X8, 20 to 50 mesh). The percolate, after suitable treatment, is passed through a similar 4-cm column to remove trace amounts of base metals, and the Rh in the second percolate is determined directly, either gravimetrically by the thiobarbituric acid method or spectrophotometrically at 470 mμ if $<$500 μg is present. Recovery of Rh is almost complete. W. J. BAKER

3750. **Precipitation of palladium dimethylglyoximate from homogeneous solution.** L. J. Kanner, E. D. Salesin and L. Gordon (Dept. of Chem. and Chem. Engng, Case Inst. of Technol., Cleveland, Ohio, U.S.A.). *Talanta*, 1961, **7** (3–4), 288–290 (in English).—Dimethylglyoxime generated in soln. from biacetyl and hydroxylamine precipitates Pd in an easily filtered form. The method is used to separate Pd from $>$200 mg of Pt and $>$1000 mg of Ni. *Procedure*—Dilute the neutral soln. (1 to 25 mg of $PdSO_4$ or $PdCl_2$) to 250 ml and add 9 ml of conc. HCl, 25 ml of biacetyl soln. containing 120 mg of biacetyl (*Ibid.*, 1960, **5**, 81) and 400 mg of hydroxyammonium chloride in 25 ml of H_2O. After 16 hr., stir for 1 hr. and filter; wash the ppt. with HCl (1:99) and then with H_2O. Dry at 110°. P. D. PARR-RICHARD

3751. **Spectrophotometric methods for the determination of osmium. I. Extraction and ultra-violet spectrophotometric determination of osmium tetroxide.** G. Goldstein, D. L. Manning, O. Menis and J. A. Dean (Anal. Chem. Div., Oak Ridge Nat. Lab., Tenn., U.S.A.). *Talanta*, 1961, **7** (3–4), 296–300 (in English).—The determination of Os in uranyl sulphate soln. by oxidation to OsO_4 and extraction with $CHCl_3$ is described. Chloride and Ru should be absent. *Procedure*—Dilute the soln. containing 0·4 to 3·3 mg of Os to 5 ml with 6N-H_2SO_4, add 5% $KMnO_4$ soln. to a permanent pink colour and discharge this with $(NH_4)_2SO_4.FeSO_4$ soln. Add 3 ml of 15M-HNO_3 and 2 ml of H_2O and extract with $CHCl_3$ (2 × 10 ml). To the combined extracts add 10 ml of 0·1M-H_2SO_4 and wash the soln. to remove HNO_3. Dilute the $CHCl_3$ layer to 25 ml and measure the extinction at 282, 289, 297, 304 or 312 mμ.

II. Extraction and determination of osmium *in situ* with 1,5-diphenylcarbazide. G. Goldstein, D. L. Manning, O. Menis and J. A. Dean. *Ibid.*, 1961, **7** (3–4), 301–306 (in English).—Quadrivalent Os in $CHCl_3$ soln. reacts with 1,5-diphenylcarbazide (**I**) to give a blue - violet product. *Procedure*—After oxidation to OsO_4 and extraction into $CHCl_3$ as described in Part I, add the washed extract to 5 ml of a 0·2% ethanolic soln. of **I** and dilute to 25 ml. After 2 hr. measure the extinction at 560 mμ; Beer's law is obeyed for 30 to 100 μg of Os. P. D. PARR-RICHARD

3752. **Determination of platinum and palladium in copper - nickel matte and ore concentrates. A fire-assay method using tin as a collector.** G. H. Faye and W. R. Inman (Dept. of Mines and Tech. Surveys, Ottawa, Canada). *Anal. Chem.*, 1961, **33** (2), 278–283.—The metals of the platinum group are collected with Sn by fusion of the sample (suitably pretreated) with a flux containing SnO_2 at 1050° for $\simeq$45 min. in a fire-assay crucible. The resulting tin button, after conversion into a spongy alloy, is dissolved in conc. HCl (any residue is collected, dissolved in 8N-HCl plus H_2O_2 and the

soln. is added to the main filtrate), the residual Sn is volatilised with conc. HCl plus conc. HBr, and any Cu, Fe and Ni are removed by cation-exchange on Dowex 50 (*cf.* Coburn, *Anal. Abstr.*, 1957, **4**, 128). The percolate is evaporated to dryness, the residue is dissolved in conc. HCl and diluted, and the Pt and Pd are separated by anion-exchange on a column (3 cm × 0·3 cm) of Amberlite IRA-400 by the method of Berman and McBryde (*Canad. J. Chem.*, 1958, **36**, 835). The Pt is determined spectrophotometrically with $SnCl_2$, or (for <100 μg) by extraction of the $SnCl_6$ complex into 5% tributyl phosphate in hexane and measurement of the extinction of the centrifuged organic phase at 350 mμ. The Pd is determined spectrophotometrically with KI (for >100 μg) or with *p*-nitrosodimethylaniline (for <100 μg). Recovery of Pt and Pd in the button is usually >98%, and the results agree well with those for the spectroscopic analysis of fire-assay beads obtained by the usual method. The behaviour of Au, Ag, Rh and Ir in the button is discussed. Leach liquors from ore processing can be treated with zinc dust to precipitate Cu, Pt and Pd for subsequent fusion with Sn.

W. J. BAKER

3753. **Infra-red spectra of some clay minerals and related structures.** B. M. Bishui and J. Prasad (Central Glass and Ceramic Res. Inst., Calcutta-32, India). *Central Glass & Ceram. Res. Inst. Bull., India*, 1960, **7** (3), 97–109.—Infra-red spectra of 16 minerals have been determined.

3754. **Spectrographic determination of the trace elements in clay with the direct-current carbon arc.** F. Hegemann, H. Kostyra and J. Kostyra (Mineral. Inst., Tech. Hochsch., München, Germany). *Ber. dtsch. keram. Ges.*, 1960, **37**, 372–377.—Full details are given for the determination of B, Ba, Be, Cr, Cu, Mn, Ni, Pb, Sn, Sr, V, Y, Zr, Ca, Mg, Fe and Ti.

J. A. SUGDEN

3755. **Fully automatic measurement of the moisture content of sands and ceramic bodies. I. By the slowing and scattering of fast neutrons.** E. Arnhein, A. Dietzel and K. Metzner (Max-Planck-Inst. f. Silikatforsch., Würzburg, Germany). *Ber. dtsch. keram. Ges.*, 1960, **37**, 311–315.—In one form of the apparatus a probe is pushed into the sample and the radiation from a Ra - Be source passes through the sample to a sensing device (BF_3 enriched with ^{10}B), which is connected to a counter. The calibration curve relating log (no. of counts per min.) and the moisture content is linear from 2 to 8% of moisture, but the sensitivity falls off rapidly below 1% of moisture. In another form of the apparatus a type of cell is used into which the sample is filled, and the sensing element uses the neutron-excited β-activity of Rh. A measured is completed in 30 sec. with an accuracy of ± 0·5%.

J. A. SUGDEN

3756. **Colorimetric and polarographic determination of some trace elements in rocks.** I. Carmichael and A. McDonald (Dept. of Geology, Imperial Coll. of Sci. & Technol., London). *Geochim. et Cosmoch. Acta*, 1961, **22** (2–4), 87–93.—Details are given for the decomposition of the rock (1 to 2 g) by means of HF - $HClO_4$ and the extraction of trace metals with dithizone after adjusting the pH of the soln. to 9·5 with an ammoniacal Na citrate - hydroxyammonium chloride buffer. Cadmium, Co, Cu, Ni, and Pb and Zn are determined colorimetrically with NaOH, tri-n-butylamine and amyl alcohol, 2,2-biquinolyl, furil α-dioxime, and dithizone in benzene, respectively. Cadmium, Cu, Pb and Zn (and Bi) may also be determined polarographically after dithizone extraction. For Sn, the rock powder (1 g) is heated with NH_4I, the sublimate is leached with N-HCl, and an aliquot is taken for the determination of Sn with gallein.

R. A. HOWIE

3757. **Apparent loss of iron during fusion of silicate materials with sodium hydroxide in nickel crucibles.** H. Bennett, R. P. Eardley and I. Thwaites (The British Ceramic Res. Ass., Queens Rd., Penkhull, Stoke-on-Trent, England). *Analyst*, 1961, **86**, 135–136.—During the analysis of aluminosilicates and materials of high Si content by fusion with NaOH in nickel crucibles an apparent loss of Fe was observed. The melt was leached with hot water and dissolved in HNO_3, and the Fe was determined spectrophotometrically with 1,10-phenanthroline. All results were low and indicated a loss of Fe proportional to the amount of Fe present. When the same samples were decomposed by HF and the F^- subsequently removed by fuming with H_2SO_4 and the Fe determined as before, the results agreed satisfactorily with the accepted values for the samples. Results obtained by fusion with NaOH lay on a straight line practically identical with a calibration graph obtained by similar fusion of standard samples. It appears therefore that the loss of Fe can be compensated for by use of a calibration graph based on fusion of standard samples. It is suggested that reduction of Fe occurs during fusion, with subsequent alloying with the nickel of the crucible.

A. O. JONES

3758. **Determination of radioactive species produced by cosmic rays in iron meteorites.** M. Honda, J. P. Shedlovsky and J. R. Arnold (School of Sci. & Engng, Univ. of California, La Jolla, U.S.A.). *Geochim. et Cosmoch. Acta*, 1961, **22** (2–4), 133–154.—Full details are given for the decomposition of octahedrite meteorites, the solvent extraction of the $FeCl_3$ acid complex into isopropyl ether, and the removal of Ni by successive pptn. with aq. NH_3, leaving Ni in soln. and giving Be, Al and Mn in the hydroxide fraction. Manganese is separated by basic H_2O_2 pptn., Be by cation exchange and elution with HCl followed by solvent extraction of the acetylacetone complex in the presence of EDTA, and Al is purified by CuS and $Fe(OH)_3$ scavenging, anion exchange with HCl, and the Gooch and Havens pptn. of $AlCl_3.6H_2O$ in HCl - ether. Potassium is separated from the ammoniacal nickel fraction by cation exchange and is pptd. as the tetraphenylborate. Chlorine is pptd. from a separate soln. as AgCl, converted into NH_4Cl and purified by sublimation. The radiochemical details for the determination of the radioactive isotopes ^{10}Be, ^{26}Al, ^{36}Cl, ^{40}K and ^{53}Mn are described: the samples are counted with a low-level β-counter, except for ^{53}Mn, the X-rays of which are measured.

R. A. HOWIE

3759. **Rapid analysis of silicate [glass] with EDTA (disodium salt).** F. I. Perchik. *Izv. Kievsk. Politekh. Inst.*, 1960, **29**, 119–121; *Ref. Zhur., Khim.*, 1960, (23), Abstr. No. 92,085.—A procedure is developed for determining Al, Fe, Ti, Ca and Mg in glass. *Procedure*—Fuse the sample (0·5 g) with NaOH, dissolve the melt in dil. HCl, evaporate the soln. to dryness, and remove SiO_2 in the usual way. Precipitate Al, Fe and Ti from the filtrate with aq. NH_3, wash the ppt. with hot water, dissolve it in hot 2N-HCl, and make up to 250 ml. To 50 ml of

the soln. add 5 ml of 0·05M-EDTA (disodium salt) (**I**) and 5 drops of 10% H_2O_2, dilute to ≃100 ml, neutralise with NaOH soln., add 20 ml of M-Na acetate and Eriochrome black T, and titrate the excess of **I** with 0·05M-$ZnSO_4$. This gives the content of total Al, Fe and Ti; Fe and Ti are determined separately colorimetrically, and the corresponding vol. of **I** soln. are calculated; the Al content is found by difference. Calcium and Mg are determined in the filtrate with **I** soln. after removal of the hydroxides of Al, Fe and Ti. The results agree well with those by gravimetric methods.

C. D. KOPKIN

3760. **Rapid analysis of slags and other materials.** V. D. Konkin and V. I. Zhikhareva (Ukraine Sci. Res. Inst. of Metals). *Zavod. Lab.*, 1961, **27** (2), 143–144.—Methods for determining Ca, Mg, Mn, Fe and Al, based on the use of EDTA (disodium salt) as titrant, are described. G. S. SMITH

3761. **Pigments for cement, magnesium oxychloride and concrete.** British Standards Institution (2 Park Street, London, W.1). B.S.1014:1961. 29 pp.—Specifications are given for a variety of inorganic pigments used in these materials.

3762. **Analysis of chromium plating baths for nitrate.** I. R. Klyachko and I. S. Schipkova (Moscow Polygraphic Inst.). *Zavod. Lab.*, 1961, **27** (2), 145.—The CrO_4^{2-} in 1 ml of the soln. are completely pptd. by addition of 5 ml of 2N-aq. NH_3 and 4 ml of 15% $BaCl_2$ soln., and the soln. is centrifuged. Portions of the colourless soln. are diluted until one drop fails to give a blue colour when mixed with one drop of diphenylamine soln. If the dilution is x, the content of NO_3^- is $x \times 0{\cdot}00197\%$.

G. S. SMITH

3763. **Analysis of gases from sulphuric acid manufacture.** S. Kh. Zarnitskiĭ. *Zavod. Lab.*, 1961, **27** (2), 138–139.—One 5-litre flask contains 110 ml of a mixture (10:1) of 5 to 10% acetaldehyde soln. and 5% furfuraldehyde soln. (for inhibiting the oxidation of SO_2) and another contains 100 ml of 3% H_2O_2 soln. Both flasks are evacuated, and the gas to be analysed is passed into the flasks simultaneously for 5 to 10 min. The contents of the first flask are titrated with K_2CrO_4 soln. in the presence of rosolic acid. The soln. in the second flask is used to give the total content of H_2SO_4 fumes, SO_2 and N_2O_3. G. S. SMITH

See also Abstracts—**3560**: *Sections I, II and III*, Determination of various elements. **3561**: *Section Va*, Electrochemical methods. *Section Vb*, Polarography. *Section VI*, Chromatographic methods. *Section VIIa*, Optical methods. **3562**: *Section VIIb*, Emission spectrographic methods. *Section VIIc*, Flame photometry. *Section VIII*, Applied analysis. **3564**, Rhodanines as reagents for metals. **3565**, Reagents for Fe and Cu. **3571**, Reduction of Ti^{4+} with silver reductor. **3812**, H_2SO_4 in presence of sulphonic acids. **3820**, V and Ni in crude oil. **3821**, Cu and Pb in reformer feedstocks. **3849**, ^{137}Cs in biol. tissues. **3912**, Microbiol. determination of As valence. **3957**, Test for Cr^{6+}. **3991**, Detection of trace metals on paper chromatograms. **3993**, Chromatography of gases extracted from metals. **4000**, Spectrographic gas identification. **4002**, Boron in steel. Tin and Sb in lead alloys. **4023**, Titration of acids and bases with metal-metal oxide electrodes. **4024**, Titration of K with Ca tetraphenylborate. **4028**, Isotopic analysis of lithium.

3.—ORGANIC ANALYSIS

Determination of elements and radicals and of organic compounds not included in other sections. Organic industrial products, including petroleum and its products, fuels, detergents, volatile oils, cosmetics, dyestuffs, fibres, plastics, resins, paints, elastomers, leather and explosives.

3764. **Quantitative organic micro-analysis.** *Farmaco, Ed. Sci.*, 1961, **16** (2), 81–164.—This special number contains the following papers: **Balances,** W. Schöniger, 81–86 (in Italian). **Preparation of substance for analysis,** W. Schöniger, 87–90 (in Italian). **Micro-analytical determination of carbon and hydrogen,** W. Schöniger, 91–99 (in Italian).—Changes in Pregl's original method and in methods for eliminating oxides of N are discussed, together with new methods for determining the products of combustion, including volumetric and gas-chromatographic methods. **Micro-analytical determination of oxygen,** W. Schöniger, 100–106 (in Italian). **Micro-analytical determination of nitrogen,** W. Schöniger, 107–115 (in Italian).—Kjeldahl and combustion methods are discussed, together with ultra-micro procedures for amounts of substance <1 mg. **Further development of the flask method in quantitative organic micro-analysis,** W. Schöniger, 116–129 (in English).—Determinations of halogens, S, P, Hg, Zn, Mg, Cd, B, As and Se are considered. **Micro-analytical determination of functional groups in organic compounds,** H. Lieb, 130–161 (in German).—The following radicals are considered—alkoxyl, carboxyl, thio-ether, *N*-alkyl, acetyl, *C*-methyl, benzoyl, carbonyl, nitro, nitroso, amino; the determination of double bonds, active H atoms and mol. wt. is also discussed.

J. I. M. JONES

3765. **Microscopic sublimation procedure for the detection and removal of impurities from organic solids.** R. H. Petrucci and J. C. Weygandt (Morley Chem. Lab., Western Reserve Univ., Cleveland, Ohio, U.S.A.). *Anal. Chem.*, 1961, **33** (2), 275–278.—In the technique described, a microscope fitted with a Kofler hot-stage and a small sublimation block is used. The sample (≃ 20 mg) is heated slowly until a liquid condensate appears on a coverglass fixed 2 to 3 mm above it. The temp. at which this occurs—"the liquid sublimation temp."—is recorded. If the identity of the impurity is known, then a quantitative determination (down to ≃0·1 mole %) can be made by the use of working curves of standard mixtures. Sublimation data are given for binary systems of nitrophenols.

G. P. COOK

3766. **Elementary organic analysis. II. Pyrolytic combustion in a rapid current of air in the presence of a catalyst.** B. Arventiev, M. Leonte and H. Offenberg. *An. Ştiinţ. Univ. "Al. I. Cuza," Iaşi, Sect. I*, 1960, **6** (1), 183–186.—Complete combustion of vapours escaping from the small tube containing the sample during the analysis is effected by passing the vapours over a catalyst composed of 20% of Co_3O_4 on asbestos at 650° to 700°. D. R. DUNCAN

3767. **Quantitative determination of the carbon-14 content of labelled material in a closed glass apparatus.** H. Kienitz and O. Riedel (Anal. Lab., Badische Anilin- & Soda-Fabrik A.-G., Ludwigshafen). *Z. anal. Chem.*, 1961, **179** (2), 93–98 (in

German).—The sample is burned in O in a Liebig tube, oxides of N are reduced to N by passage over heated copper and the CO_2 is collected and measured in a vacuum apparatus. The CO_2 is then diluted (1:4) with methane and counted in a proportional counter. T. R. ANDREW

3768. **Titrimetric methods for the micro-determination of halogens in organic compounds by the rapid combustion procedure. I. Determination of individual halogens.** J. E. Fildes and A. M. G. Macdonald (Univ., Birmingham, England). *Anal. Chim. Acta*, 1961, **24** (2), 121–127 (in English).—In the absence of N and S, Cl or Br is determined by titration of the HCl or HBr formed on absorption in 0·01N-NaOH. When S and/or N is present the absorption and titration are completed as above and the mercuric oxycyanide method of Belcher *et al.* (*Anal. Abstr.*, 1954, **1**, 2696) or the mercurimetric method of Cheng (*Anal. Abstr.*, 1960, **7**, 3286) is applied. In an alternative method for Br in the presence of S and/or N, the gases are absorbed in N-NaOH containing SO_3^{2-}, the soln. is boiled with H_2O_2, neutralised with N-H_3PO_4 and heated with NaClO soln. The excess of NaClO is reduced with Na formate and the bromate formed is titrated iodimetrically. Iodine is determined, after absorption in N-NaOH, by neutralising the soln. with N-H_3PO_4 to methyl red, adding bromine water, destroying the excess of Br with formic acid, adding 2N-H_2SO_4 and KI and titrating the liberated iodine with 0·02N-$Na_2S_2O_3$. This method can be used when S and/or N is present. H. N. S.

3769. **Semi-micro determination of fluorine in organic compounds.** C. A. Johnson and M. A. Leonard (Anal. Develop. Group, Standards Dept., Boots Pure Drug Co. Ltd., Nottingham, England). *Analyst*, 1961, **86**, 101–104.—The sample (5 to 25 mg) enclosed in filter-paper is burnt in an oxygen flask containing water. When combustion is complete the flask is set aside for 10 min., with occasional shaking. The liquid is diluted to 250 ml and to an aliquot ($\simeq \equiv 25$ μg of F^-) are added 10 ml of alizarin complexan (1,2-dihydroxyanthraquinon-3-ylmethylamine-*NN*-diacetic acid) and 3 ml of an acetic acid - Na acetate buffer soln. (pH 4·6). After mixing, 10 ml of 0·005M-$Ce(NO_3)_3$ is added and the soln., diluted to 100 ml, is set aside, protected from light, for 1 hr. The extinction is measured at 610 mμ against a reagent blank and referred to a calibration graph. Liquid samples can be satisfactorily burnt in a gelatin or, preferably, a methylcellulose capsule containing $\simeq$30 mg of cellulose powder. Soln. derived from the combustion of samples containing S are boiled with H_2O_2, phenol and N-NaOH (1 ml in excess of neutrality) are added and, after removal of H_2O_2 by boiling, the pH is adjusted to $\simeq$4 with N-HCl. Aluminium and Fe^{3+}, and PO_4^{3-} (if present in large excess), interfere. A. O. JONES

3770. **Application of the flask-combustion technique to sulphur-containing substances.** C. Vickers and J. V. Wilkinson (Standards Dept., Boots Pure Drug Co. Ltd., Nottingham). *J. Pharm. Pharmacol.*, 1961, **13** (2), 72–74.—The flask-combustion technique of Johnson and Vickers [*Ibid.*, 1959, **11** (Suppl.), 218T] followed by direct alkalimetric titration or $Ba(ClO_4)_2$ titration (Fritz and Yamamura, *Anal. Abstr.*, 1956, **3**, 389) can be used for the assay of a number of S-containing materials of pharmaceutical and horticultural interest, including tablets and ointments. The results agree with those obtained by established methods. The alkalimetric method is suitable only for samples that do not yield acidic (other than H_2SO_4) or basic substances on combustion, and the $Ba(ClO_4)_2$ technique is not satisfactory for the determination of S in organic compounds that contain a high proportion of N. A. R. ROGERS

3771. **Amperometric titration of sulphydryl [mercapto] and disulphide groups with organic mercury compounds at the rotated dropping-mercury indicator-electrode.** W. Stricks and S. K. Chakravarti (Dept. of Chem., Marquette Univ., Milwaukee, Wis., U.S.A.). *Anal. Chem.*, 1961, **33** (2), 194–199.—An accurate and rapid method for the determination of 6 to 120 μg of mercapto-groups in amino-acids, peptides and proteins is described. Ethylmercury chloride is superior to phenylmercury hydroxide as titrant and the accuracy of the method is $\pm$0·5%. Its disadvantage is the purification and cost of ethylmercury chloride. C. B. BAINES

3772. **Amperometric, argentimetric and mercurimetric titration of sulphydryl [mercapto-groups]. I. Amperometric titration.** I. M. Kolthoff and J. Eisenstädter (Sch. of Chem., Univ. of Minnesota, Minneapolis, U.S.A.). *Anal. Chim. Acta*, 1961, **24** (1), 83–90 (in English).—Titrations of cysteine,, glutathione, thioglycollic acid and ethanethiol at a rotating platinum-wire electrode in ammonia buffers are discussed in relation to the results of other workers. Cysteine gives high results except at concn. of 2·5 to 5 $\times$ 10^{-5}M in the presence of 0·1M-Na_2SO_3. Good results are obtained for glutathione and ethanethiol, and the titration is unaffected by the presence of sulphite. Thioglycollic acid behaves similarly to cysteine, giving high results, but in the presence of 0·1M-Na_2SO_3 at concn. $< 5 \times 10^{-4}$M the error is $< 2\%$. A. C. R. HARTLEY

3773. **Investigation of the micro-analysis of gases by evaporation curves.** N. M. Barÿshova. *Trudÿ Komiss. Anal. Khim., Akad. Nauk SSSR*, 1960, **10**, 225–237; *Ref. Zhur., Khim.*, 1960, (24), Abstr. No. 96,101.—The method of evaporation curves, which has been successfully used for the analysis of hydrocarbon gases with liquid-nitrogen cooling of the mixture, can be used for the analysis of binary mixtures of the vapour of liquid normal paraffins. The analysis of binary mixtures of isomers is hardly possible by this method without reducing the working temperatures (*e.g.*, with liquid hydrogen). The method of evaporation curves can be used to determine the composition of mixtures of pentane and hexane, and of hexane and octane. Because of the low vapour pressure of heptane at its melting-point, the method of evaporation curves cannot be used (it does not permit measurement of pressures $< 10^{-3}$ torr). If the components of the binary mixture differ by two or more CH_2 groups, any such mixture can be analysed by this method without difficulty. The method of evaporation curves can be used in certain cases for the partial study of phase diagrams of volatile systems on the micro scale. C. D. KOPKIN

3774. **Gas-chromatographic separation of low-boiling hydrocarbons using active alumina as support for the liquid phase.** I. Halász and E. E. Wegner (Inst. für Phys. Chem., Univ. Frankfurt/Main, Germany). *Nature*, 1961, **189**, 570–571.—The saturated and ethylenic hydrocarbons from C_1 to C_4 have been separated with H as carrier gas at 0°

on a column of 18% of 3,3′-oxydipropionitrile supported on 100 to 150-mesh alumina calcined at 400° for 9 hr. Similar results were obtained with squalane or triethylene glycol as stationary phase. The performance of columns with alumina as support was superior to that of columns with an inactive support. A. R. ROGERS

3775. **Method for determining total hydrocarbons dissolved in water.** A. H. Wehe and J. J. McKetta (Dept. of Chem. Engng, Univ. Texas, Austin, U.S.A.). *Anal. Chem.*, 1961, **33** (2), 291–293.—The method described is based on Henry's law and assumes that the gas is in equilibrium with the water at some conditions of elevated temp. and pressure, and that a sample can be withdrawn from the equilibrium cell without disturbing the state of the equilibrium. Results are accurate to within ±5%. The procedure was applied to the butane - but-1-ene - water system. G. P. COOK

3776. **Physical procedures for the analysis of mixtures of polychloroethanes.** J. S. Ratcliffe (Newcastle Coll., Tighe's Hill, N.S.W., Australia). *Anal. Chim. Acta*, 1961, **24** (1), 2–4 (in English).—Seven polychloroethanes were separated into binary mixtures by the combined technique of continuous fractionation and total reflux with intermittent take-off. The recovery was 98%. Subsequent analysis by refractive-index measurements gave an accuracy of 0·5 to 2·0%. A linear relationship exists between component mass fraction and refractive index of a binary mixture. The variation of refractive index with temperature was studied. A. C. R. HARTLEY

3777. **Rapid determination of water in ethanol by near-infra-red spectrophotometry.** P. Ferrer Pi and L. Condal-Bosch. *Afinidad*, 1960, **17**, 280–286.—Two methods are described. *Method of dilution in CCl_4 (for water contents of 0 to 9%)*—After dilution of the sample with five times its vol. of CCl_4, the extinctions are measured at 1·735, 1·87 and 1·89 μ, with a path length of 0·2 to 1·0 cm. The water content of the sample can then be calculated from $E_{1\cdot89} - E_{1\cdot87}/E_{1\cdot735} - E_{1\cdot87}$ and reference to the table given. *Direct method (for water contents of 0 to 2%)*—The extinctions of the sample are measured in a 1-cm cell at 1·95 μ and at the point of maximum absorption (close to 1·87 μ). The difference between these readings is referred to the table given. L. G. L. UNSTEAD-JOSS

3778. **Colorimetric determination of soluble carbohydrates with copper reagents and heteropoly-acids.** V. N. Khrustaleva and V. V. Kozlov. *Nauch. Rabot. Moskov. Inst. Narod. Khoz.*, 1959, (15), Part 2, 128–137; *Ref. Zhur., Khim., Biol. Khim.*, 1961, (2), Abstr. No. 2S29.—Tests were carried out to confirm the accuracy of a colorimetric determination of sol. carbohydrates by oxidising them with copper reagents and soln. of Cu_2O in molybdo- or tungstophosphoric acid (concn. range for glucose and fructose, 0·025 to 0·2 g per litre; for maltose <0·125 g per litre; and for lactose <0·15 g per litre). In the presence of a large amount of sucrose, tungstophosphoric acid is used. Lactose, maltose and sucrose in concn. of <0·25 g per litre do not affect the determination of glucose. K. R. COOK

3779. **Analysis of sugar mixtures by gas - liquid partition chromatography.** S. W. Gunner, J. K. N. Jones and M. B. Perry (Dept. of Org. Chem., Queen's Univ., Kingston, Ontario, Canada). *Chem. & Ind.*, 1961, (8), 255.—Glycose mixtures are converted into their fully acetylated glycitol derivatives, and samples (2 to 5 μg) are separated on the column at 190°, with Ar as carrier gas, at a flow rate of 60 and 130 ml per min. Retention times are recorded with an ionisation detector and the molar ratios of the glycoses are determined by measuring the areas under the peaks of the curve. Erythritol is used as an internal standard. This method is very sensitive to minor components and its accuracy is similar to that of older methods. A. C. R. HARTLEY

3780. **Absence of an isotope effect in the fractional recrystallisation of α-D-[1-^{3}H]glucose.** H. S. Isbell, H. L. Frush and N. B. Holt (Nat. Bureau of Standards, Washington, D.C., U.S.A.). *Anal. Chem.*, 1961, **33** (2), 225–226.—The fractional recrystallisation of both α-D-[1-^{3}H]glucose and α-D-[6-^{3}H]-glucose is described. No indication of any isotope effect is observed for either substance. C. B. BAINES

3781. **Determination of higher-molecular-weight aliphatic aldehydes and ketones.** A. P. Altshuller and I. R. Cohen (Air Pollution Engng Res., Robert A. Taft Sanitary Engng Center, Cincinnati, Ohio, U.S.A.). *Anal. Chim. Acta*, 1961, **24** (1), 61–66 (in English).—The aldehyde or ketone is dissolved in 2-methoxyethanol - H_3PO_4 (3:1) and treated for 4 hr. at 35° with a 2% soln. of *p*-nitrophenyldiazonium fluoroborate in 2-methoxyethanol. The absorption spectra show that the maxima of higher aldehydes and ketones are more intense than those of formaldehyde and acetone, and the method has been used to analyse for propionaldehyde in their presence. The maxima occur in the ranges 380 to 395 mμ and 440 to 460 mμ. The latter are less suceptible to interference from phenols and diolefins. The reaction products are discussed. A. C. R. HARTLEY

3782. **X-ray powder-diffraction data for 2,4-dinitrophenylhydrazones of aldehydes and ketones.** L. D. Calvert and M. Przybylska (Div. of Appl. Chem., Nat. Res. Council, Ottawa, Canada). *Appl. Spectroscopy*, 1961, **15** (2), 39–45.—To facilitate the identification of carbonyl compounds, the spacing and intensities of the three strongest lines are listed (in order of Hanawalt groups) for 103 2,4-dinitrophenylhydrazones of aldehydes and ketones. The X-ray powder-diffraction patterns of 64 of these compounds were determined; the data for the remainder were taken from the literature. W. J. BAKER

3783. **Paper chromatography in fat analysis. The reduction of carbonyl compounds on the paper.** H. P. Kaufmann and H. J. Hennig (Dtsch. Inst. für Fettforsch., Münster, Germany). *Mikrochim. Acta*, 1961, (2), 333–342 (in German).—Fatty aldehydes, ketones and keto-acids can be reduced to the corresponding alcohols by treating the mixture of compounds at the starting point of the chromatogram with $LiBH_4$ or $NaBH_4$ in tetrahydrofuran. After 2 hr. at room temp., the excess of borohydride is destroyed with water and the chromatogram is developed in the normal manner. Olefinic, *i.e.*, C:C, bonds and ester groupings are not attacked. W. T. CARTER

3784. **Formaldehyde solution.** British Standards Institution (2 Park Street, London, W.1). B.S.

2942:1957. Amendment No. 1 (7.4.61). 2 pp.—A new figure showing the relationship between sp. gr. (25°/25°) and composition is published.

3785. **Detection of ketones via oxidation to esters.** R. Drucker and M. J. Rosen (Dept. of Chem., Brooklyn Coll., N.Y., U.S.A.). *Anal. Chem.*, 1961, **33** (2), 273–275.—Ketones are detected and distinguished from saturated aliphatic aldehydes by oxidation with peroxytrifluoroacetic acid. The esters and/or lactones produced only by the ketones are detected by the characteristic purple - red colour of the ferric hydroxamate test. All the ketones tested, except acetone, gave a positive test (sensitivity $\simeq$2·5 mg). Esters must be absent from the sample before oxidation.

G. P. Cook

3786. **Determination of tartaric acid and tartrates by lead tetra-acetate.** A. Berka (Charles Univ., Prague, Czechoslovakia). *Anal. Chim. Acta*, 1961, **24** (2), 171–174 (in French).—The tartrate radical is oxidised quant. to CO_2 by an excess of Pb tetra-acetate in a medium of 80% acetic acid containing K acetate. The soln. for analysis should contain the equiv. of $\simeq$5 ml of 0·01M-tartaric acid dissolved in 10 ml of glacial acetic acid and 5 ml of 20% aq. K acetate. It is mixed with 10 ml of 0·05M-Pb tetra-acetate in acetic acid and, after 30 min., the excess of Pb tetra-acetate is titrated potentiometrically with 0·05M-quinol in 1% H_2SO_4 (Berka and Zýka, *Anal. Abstr.*, 1959, **6**, 815). The method is recommended for the analysis of Bi tartrate and the complex tartrates of Bi and Na, K or Li.

H. N. S.

3787. **Determination of the acid chloride content of carboxylic acid chloride samples.** K. Burger and E. Schulek (L. Eötvös Univ., Budapest, Hungary). *Magyar Kém. Foly.*, 1961, **67** (2), 59–62.—In the method described, both the carboxylic acid chloride and the hydrolysis products (free carboxylic acid and HCl) usually present in a sample of carboxylic acid chloride are determined. The sample is treated with absolute ethanol to form the ethyl ester, and is then titrated with standard alkali, first to a methyl red end-point, and then to phenolphthalein. The ester content of the soln. is subsequently found by saponification with a known excess of hot alkali and back-titration of this excess with standard H_2SO_4 soln. Examples of application of the method to the chlorides of palmitic and stearic acids are given. For the determination of acetyl chloride, the method is slightly modified. Full details of procedure and calculation are given.

B. Vaszko

3788. **Conductimetric titration of metal acetates in aqueous medium.** F. Gaslini and L. Z. Nahum (Res. Dept., Cartiera Vita Meyer and Co., Milan, Italy). *Anal. Chim. Acta*, 1961, **24** (1), 79–82 (in English).—Mono- and bi-valent metal acetates can be titrated conductimetrically with trichloroacetic acid in an atmosphere of N at room temperature. Fifteen metal acetates have been titrated, and sharp end-points were obtained. The method may be applied to salts of acids weaker than acetic by dissolving them in excess of aqueous acetic acid.

A. C. R. Hartley

3789. **Assay of sodium citrate and sodium potassium tartrate by cation exchange and non-aqueous titrimetry.** M. L. Richardson (John and E. Sturge Ltd., Lifford Chemical Works, Kings Norton, Birmingham, England). *Anal. Chim. Acta*, 1961, **24** (1), 46–54 (in English).—*Determination of anion*—Aqueous soln. are passed through a column of cation-exchange resin [Amberlite IR-120 (H^+ form)]. The percolate and aqueous washings are concentrated and titrated with 0·1N-NaOH, with thymol blue as indicator for citrate and phenolphthalein for tartrate. *Determination of cation*—Sodium citrate is dissolved in glacial acetic acid and titrated potentiometrically with standard acetous $HClO_4$ (0·1N). Sodium potassium tartrate is stirred for 20 min. with a known vol. of standard acetous $HClO_4$ soln., and the excess of acid is back-titrated potentiometrically with acetous Na acetate (0·1N) or acetous K acetate soln. The accuracy is comparable with that of the B.P. method.

A. C. R. Hartley

3790. **High-resolution mass spectra of aliphatic esters.** J. H. Beynon, R. A. Saunders and A. E. Williams (Dyestuffs Div., I.C.I. Ltd., Manchester, England). *Anal. Chem.*, 1961, **33** (2), 221–225.—Data for 27 compounds are presented. Assignment of a formula to each fragment ion in the spectra makes it easier to identify a compound from its spectrum and to distinguish an ester from compounds such as isobaric alcohols, ethers and acids.

G. P. Cook

3791. **Micro-determination of primary and secondary saturated nitro-compounds.** V. A. Klimova and K. S. Zabrodina (N. D. Zelinskyi Inst. Org. Chem., Acad. Sci., USSR). *Izv. Akad. Nauk SSSR*, 1961, (1), 176–177.—*Procedure*—Dissolve the sample (2 to 5 mg) in 3 ml of KOH soln. (2% in 80% ethanol) in a 150-ml flask. After 10 min. add 50% aq. KI soln. (3 ml) and then 15% HCl (5 ml). Stopper the flask, shake, and set aside in the dark for 10 min. Add H_2O (50 ml) and titrate the liberated iodine with 0·01N-$Na_2S_2O_3$, with starch as indicator.

J. W. Price

3792. **Rapid method for the detection and identification of quaternary ammonium salts.** J. Bastianutti (Lab. Chim. Prov., Udine, Italy). *Boll. Lab. Chim. Provinciali*, 1960, **11** (4), 693–696.—Chromatography on Whatman No. 1 paper is used, with a mixture of acetone, water and 0·04% bromophenol blue soln. (2:2:1) as mobile phase. The sample is applied to the paper from soln. in n-butanol and separation is achieved in 2 to 3 hr. by the ascending technique. R_F values for a number of commerical products are quoted. As little as 0·001 mg can be detected.

E. C. Apling

3793. **Polarography of quaternary ammonium compounds.** B. C. Southworth, R. Osteryoung, K. D. Fleischer and F. C. Nachod (Rensselaer Polytech. Inst., Troy, N.Y., U.S.A.). *Anal. Chem.*, 1961, **33** (2), 208–212.—Electrolytic reductions of compounds, the quaternary ion acquires an electron in two ways. In the first, simple aliphatic compounds, the quaternary ion acquires an electron to form a neutral entity which subsequently reacts with water to form hydrogen and the quaternary hydroxide. In the second type of reaction, the neutral entity may break down into a tertiary amine and a hydrocarbon, or two molecules may rearrange to form a bis-compound. This type of reaction is found in compounds having an aromatic or pyridinium group. Polarographic procedures that are suitable for the determination of quaternary compounds are limited in their application to those compounds with a reduction potential less negative than −1·9 V.

G. P. Cook

3794. Determination of the composition of urea - hydrocarbon complexes. R. W. Kiser, M. D. Shetlar and G. D. Johnson (Dept. of Chem., State Univ., Manhattan, Kans., U.S.A.). *Anal. Chem.*, 1961, **33** (2), 314–315.—Urea can be quant. pptd. from these complexes by the addition of xanthhydrol. *Procedure*—Dissolve the sample (50 mg) in 8·7N-acetic acid (100 ml) and add 5 ml of a clear saturated soln. of xanthhydrol in methanol. Set the mixture aside for several hours, collect the ppt. on a weighed sintered-glass disc, wash it well with a saturated soln. of dixanthhydrylurea in methanol, dry it for 2 hr. at 100° and weigh. The max. relative error is 0·2%. W. J. BAKER

3795. Acid-catalysed acetylation. Determination of ketoximes and *vic.*-dioximes. G. H. Schenk (Chem. Dept., Wayne State Univ., Detroit, Mich., U.S.A.). *Anal. Chem.*, 1961, **33** (2), 299–302.—Acetylation is carried out at room temp. in pyridine soln. in the presence of $HClO_4$ as catalyst. The acetic anhydride in the blank and after reaction with the sample is determined by hydrolysis, with a minimum of H_2O, to acetic acid, and titration with alcoholic base soln. The method is applicable to the determination of ketoximes, some aldoximes, and benzophenone hydrazone, and supplements the method of Banks and Richard (*Anal. Abstr.*, 1960, **7**, 1415). G. P. COOK

3796. Perchloric acid titration of bases that contain mercapto- or sulphide groups. I. Bayer and E. Posgay (Lab. d. Ungarischen Pharmakopöekommission, Budapest). *Pharm. Zentralh.*, 1961, **100** (2), 65–71.—Basic compounds containing −SH or =S groups can be titrated with $HClO_4$ in acetic acid in the presence of mercuric acetate (**I**) with an accuracy of $\simeq \pm 0{\cdot}5\%$. *Procedure*—For thiourea and thiosinamine, dissolve the sample (1 milli-equiv.) in glacial acetic acid (20 ml) and titrate with 0·1N-$HClO_4$, with gentian violet (**II**) as indicator. During the titration, add 1-ml portions of a 3% soln. of **I** in acetic acid (5 or 6 ml in all) so as to maintain a slight excess of **I**; a large excess, which would cause pptn., must be avoided. For Na thialbarbitone, determine Na by titration of a soln. of the sample (60 to 80 mg) in acetic acid (5 ml) with 0·1N-$HClO_4$ to the blue - green colour of **II**; to determine the total alkalinity, add a soln. of **I** (2 g) in acetic acid (30 ml) and continue the titration with 0·1N-$HClO_4$ to a yellow - green colour, then titrate to a full blue colour with 0·1N-K acetate in acetic acid. For disulfiram, dissolve the sample (50 to 60 mg) in $CHCl_3$ (30 ml), add acetic anhydride (30 ml) and a 3% soln. of **I** in acetic acid (10 ml), titrate with 0·1N-$HClO_4$ to the yellow - green colour of **II** and then with 0·1N-K acetate to a full blue colour. A. R. ROGERS

3797. Iodimetric estimation of water-soluble dithiocarbamates. M. L. Shankaranarayana and C. C. Patel (Dept. of Inorg. and Phys. Chem., Indian Inst. Sci., Bangalore 12). *Z. anal. Chem.*, 1961, **179** (4), 263–266 (in English).—The oxidation product (thiuram disulphide) which interferes with the iodimetric titration, may be removed by extraction with organic solvents. *Procedure*—Neutralise a 0·5 to 1·5% dithiocarbamate soln. (10 ml) with 0·1N-acetic acid to phenolphthalein. Titrate with 0·025N-iodine until a brownish-yellow colour appears. Add light petroleum (50 ml), shake, then add water (50 ml) and fresh starch soln. (1 ml) and continue the titration to a permanent blue colour. A glass capillary connected with the tip of the burette is used to deliver the iodine soln. below the light petroleum layer. The error of 15 determinations was within ±0·56%. Satisfactory results were also obtained with CCl_4 and $CHCl_3$ as solvents. A. J. BENNETT

3798. Amperometric and polarographic determination of allyl isothiocyanate. W. Fürst (Inst. f. Pharmazie u. Lebensmittelchem., Friedrich-Schiller-Univ., Jena, Germany). *Pharm. Zentralh.*, 1961, **100** (2), 71–77.—Allylthiourea (**I**) (2 to 10 mg) is determined by titration in aq. NH_3 - NH_4NO_3 buffer soln. with 0·01N-$AgNO_3$ with amperometric detection of the end-point (dropping-mercury electrode at −0·6 V *vs.* the N.C.E.). Smaller quantities (0·2 to 2 mg) are determined polarographically by measurement of the wave at −0·38 V *vs.* the N.C.E. in 0·1N-NaOH. Allyl isothiocyanate is determined after conversion into **I** by heating with 25% aq. NH_3 for 10 min. at 40°. The method has been applied to the determination of allyl isothiocyanate in mustard seed; isolation by distillation is not necessary. A. R. ROGERS

3799. Volumetric determination of dixanthogen. M. L. Shankaranarayana and C. C. Patel (Dept. of Inorg. and Phys. Chem., Indian Inst. of Sci., Bangalore). *Analyst*, 1961, **86**, 98–101.—The dixanthogen [*e.g.*, dibutyl dixanthogen (prep. described)] is heated at 40° to 50° for ≃ 25 min. with 5 ml of 10% NH_4NO_3 soln., 10 ml of 2% KCN soln. and 10 ml of acetone. The cooled liquid is shaken with benzene to remove the yellow xanthogen monosulphide, and the aq. layer containing an equiv. amount of KSCN is acidified with H_3PO_4 and heated on a water bath to remove HCN. Bromine is added to the cooled liquid until its colour persists, and the excess is removed with solid $FeSO_4$. After addition of 3 g of KI and some $NaHCO_3$, the stoppered vessel is set aside in the dark for 10 min. and then the iodine liberated by reaction of SCN^- with CNBr is titrated with 0·05N-$Na_2S_2O_3$, with starch as indicator (1 ml ≡ 0·14925 g of dibutyl dixanthogen). The method is applicable in the presence of xanthate. A. O. JONES

3800. Infra-red spectra of some organophosphorus extractants. C. A. Horton and J. C. White (Anal. Chem. Div., Oak Ridge Nat. Lab., Tenn., U.S.A.). *Talanta*, 1961, **7** (3–4), 215–231 (in English).—I.r. spectra on CCl_4 or CS_2 soln. of 12 organophosphorus compounds (possible extractants of metal ions), together with those of certain impurities or degradation products, were determined. The results were used to clarify or confirm the structure of the compounds, since several absorption bands could be assigned to definite groups within the molecules. P. D. PARR-RICHARD

3801. Gasometric determination of alkyl radicals in polyalkylsiloxanes and other organosilicon compounds. M. G. Voronkov and V. T. Shemyatenkova (Inst. Silicate Chem., Acad. Sci., USSR). *Izv. Akad. Nauk SSSR*, 1961, (1), 178–180.—An apparatus is described for the determination of methyl and ethyl radicals by heating the sample (0·1 to 0·15 g) with powdered KOH (3 g) for 2 hr. at 250° to 270° and measuring the amount of gaseous hydrocarbon evolved. An accuracy of 1 to 2% is obtained. J. W. PRICE

3802. Analysis of the products of direct synthesis of alkylchlorosilanes. A. P. Kreshkov, V. A. Bork and L. A. Shvȳrkova (D. I. Mendeleev Moscow

Chem.-Tech. Inst.). *Zavod. Lab.*, 1961, **27** (2), 147–149.—The determination of methyltrichlorosilane is based on gravimetric or turbidimetric determination of the insol. polymer of three-dimensional structure formed after hydrolysis with water. The other methylchlorosilanes yield liquid polymers of linear structure. The determination of H-containing methylchlorosilanes is based on oxidation by $KMnO_4$ of the ≡SiH bond and that of $SiCl_4$ is based on its reaction with MoO_4^{2-} to give a heteropoly-acid, which is determined colorimetrically. G. S. SMITH

3803. **Polarographic determination of carcinogenic hydrocarbons.** K. Schwabe and G. Schneider (Inst. Elektrochem. u. Phys. Chem., Tech. Hochsch., Dresden). *Z. Chem.*, 1961, **1** (2), 50–53.—Compounds examined were anthracene, perylene, benzo[*a*]pyrene, 9,10-dimethyl-1,2-benzanthracene and 1,2:5,6-dibenzanthracene. Ethanol and dioxan were used as solvents and tetrabutylammonium iodide and hydroxide as supporting electrolytes. A pH range of 5·7 to 11·9 was covered by mixing these two. Each compound investigated gave 2 waves. Reduction mechanisms and variables such as pH and temp. are discussed. The lower limit for quant. determination was 1 to 2×10^{-4}M, and the coeff. of variation at 10^{-4}M ranged from 2·4% for 9,10-dimethyl-1,2-benzanthracene to 5·8% for anthracene. The method is about as sensitive as i.r. absorption, but less than u.v. fluorescence. Smaller vol. can be used with u.v. fluorescence, so that the absolute wt. is about the same. The chief disadvantage is the need for extremely pure soln., not easily achieved with blood extracts.
G. RUSSELL

3804. **Gradient elution in the separation of chlorophenols by ion exchange.** N. E. Skelly (Dow Chemical Co., Midland, Mich., U.S.A.). *Anal. Chem.*, 1961, **33** (2), 271–273.—The separation of the isomers of tetrachlorophenol from each other and from pentachlorophenol on Dowex 2-X8 resin (acetate form) by gradient elution with acetic acid in methanol is described. Concn. of the chlorophenols in the eluate are determined by u.v. spectrophotometry. The method was applied to the analysis of commercial pentachlorophenol.
G. P. COOK

3805. **Determination of diazophenols by reduction with bivalent salts of vanadium.** A. A. Nemodruk and V. F. Oreshko. *Izv. Vyssh. Ucheb. Zavedenii, Khim. i Khim. Tekhnol.*, 1960, **3** (2), 316–319; *Ref. Zhur., Khim.*, 1960, (22), Abstr. No. 88,371.—One mole of diazophenol (**I**) is reduced by two moles of VSO_4. *Procedure*—Add conc. HCl (20 to 25 ml) and 0·5% safranine soln. (3 to 4 drops) to **I** (0·2 to 0·4 g), displace the air with CO_2 or N and add ≃0·1N-VSO_4 (50 ml). Pass CO_2 or N for a further 5 min., and titrate the excess of VSO_4 with 1·0 N-$(NH_4)_2SO_4.Fe_2(SO_4)_3$ to a colour change from green to lilac, maintaining the gas flow throughout. Titrate a VSO_4 blank soln. under the same conditions. The following compounds were determined: 2-diazophenol and its monosulphonic acid and mono- and di-chloro-derivatives, 1-diazo-2-naphthol and 2-diazo-1-naphthol, 1-diazo-2-napththol-3-carboxylic acid, 1-diazo-2-naphthol-4-sulphonic acid and 1-diazo-6-nitro-2-naphthol-4-sulphonic acid. The method is superior in simplicity, accuracy and reproducibility to other methods used in the determination of **I**. K. R. COOK

3806. **Polarographic determination of vanillin.** J. Davídek (Inst. f. Lebensmittel-Chem. u. -Untersuchung, Chem.-tech. Hochsch., Prague, Czechoslovakia). *Z. anal. Chem.*, 1961, **179** (3), 165–169 (in German).—Condensation of vanillin with hydroxylamine at pH 5·9 gives vanillin oxime, which is more suitable for polarographic analysis than vanillin. At a half-wave potential of −0·93 V the oxime gives a well-developed wave which is twice as high as the vanillin wave, and remains unchanged for 3 hr. *Procedure*—To a vanillin or vanilla sugar soln. (1 to 5 ml) add phosphate buffer soln. (pH 5·9) (4 ml) and M-hydroxyammonium chloride (1 ml), and dilute to 10 ml. After removing O, record the polarogram. For pure vanillin use a standard curve; for vanilla sugar use the method of standard addition to eliminate the effect of sugar on the height of the oxime wave. The sensitivity is twice that of the direct polarographic method. The mean error is ±2·6% (7 determinations).
A. J. BENNETT

3807. **Infra-red absorption spectra of some aromatic hydroxyketones.** N. M. Cullinane, R. A. Woolhouse and V. V. Bailey-Wood (Univ. Coll., Cardiff, Wales). *Rec. Trav. Chim. Pays-Bas*, 1961, **80** (2), 116–120.—The i.r. spectra of some hydroxyacetophenones, hydroxybenzophenones and hydroxyacetonaphthones have been measured. N. E.

3808. **Determination of cumene hydroperoxide and acetophenone by oscillographic polarography.** Yu. V. Vodzinskiĭ and I. A. Korshunov. *Trudy Khim. i Khim. Tekhnol.*, 1959, (2), 362–365; *Ref. Zhur., Khim.*, 1960, (20), Abstr. No. 80,885.—A rapid method is described for the determination of acetophenone (**I**) and cumene hydroperoxide (**II**) when present together (with a ratio of concn. of **I** to **II** of up to 1:70) by oscillographic polarography with a dropping-mercury electrode. *Procedure*—Dissolve 100 mg of sample in 5 ml of basal soln. (N-LiCl in 50% isopropyl alcohol) and polarograph with $V_{const.} = 1·7$ V and $V_{var.} = 0·7$ V, finding the content of **I** from a calibration curve. The non-linearity of the dependence of the current on the concn. of **I** is due to adsorption of the reduction products of **I** on the dropping-mercury electrode. Make 1 ml of the same soln. up to 5 ml with the basal soln. and polarograph with $V_{const.} = 0·9$ V and $V_{var.} = 0·7$ V to find the content of **II**. The analysis of one sample takes 15 min. The relative error of the method is ≯±5%. C. D. KOPKIN

3809. **The detection of 2′-hydroxychalcones with boron compounds. I. Boron trifluoride.** R. Neu (Firma Dr. Willmar Schwabe G.m.b.H., Karlsruhe, Germany). *Mikrochim. Acta*, 1961, (2), 206–213 (in German).—Stable characteristic colours are obtained from 2′-hydroxychalcones by exposing a filter-paper impregnated with a soln. of the chalcone in ethanol to the vapour of boron trifluoride-diethyl ether. An improved reagent that does not fume in air can be obtained by replacing the ethyl ether by tetrahydrofuran. The colours given by a number of chalcones on the CIE (Commission Internationale de l'Éclairage) system are tabulated. W. T. CARTER

3810. **Extraction of nitrophenols from aqueous solutions by anion-exchange resins.** A. B. Davankov, L. B. Zubakova and N. A. Shabanova. *Zhur. Prikl. Khim.*, 1961, **34** (2), 403–407.—Weakly and strongly basic anion-exchange resins were examined

in a study of the conditions of sorption of *p*-nitrophenol, 2,4-dinitrophenol and 2,4,6-trinitrophenol from aq. soln. Anionite MBP (2-methyl-5-vinylpyridine) was tested with either TGM-3 (the dimethacrylic ester of triethylene glycol) or DVB (divinylbenzene) in the ratio of 50:3. It was found that the anionites examined have a high adsorptive power (up to 9 milli-equiv. per g) for nitrophenols. A. BURWOOD-SMITH

3811. **Mercurimetric estimation of thiols, aryl trityl sulphides and disulphides.** D. C. Gregg, P. E. Bouffard and R. Barton (Dept. of Chem., Univ. Vermont, Burlington, U.S.A.). *Anal. Chem.*, 1961, **33** (2), 269–271.—Thiols and aryl trityl (triphenylmethyl) sulphides are specifically titrated with Hg^{2+}, with diphenylcarbazone as the indicator. Disulphides, non-trityl sulphides, sulphoxides and sulphones do not interfere, but many disulphides can be determined by reduction and titration of the resulting thiols. The reproducibility and accuracy are within ± 2·5%. G. P. COOK

3812. **Determination of sulphuric acid and sulphonic acids in mixtures by differential titration in acetone medium.** E. A. Gribova (K. E. Voroshilov Sci. Res. Inst. of Org. Intermediates and Dyestuffs). *Zavod. Lab.*, 1961, **27** (2), 154–157.—The method previously described (Gribova *et al.*, *Anal. Abstr.*, 1959, **6**, 2936) is modified by the use of 0·1N-tetraethylammonium hydroxide in a mixture of benzene and ethanol (2:1) as titrant, and mixed indicators, neutral red and thymolphthalein, to give visual end-points. G. S. SMITH

3813. **Polarographic titration of sodium quinolsulphonate with iodine.** J. Šimek (Fac. Electrotech., Inst. Technol., Prague). *Chem. Průmysl*, 1961, **11** (2), 82–83.—*Procedure*—To 10 ml of the sample soln. ($\simeq 4 \times 10^{-4}$M) add H_2O (100 ml) and acetate buffer soln. (300 g of cryst. Na acetate plus 900 ml of H_2O plus 1 ml of anhyd. acetic acid) (10 ml) and titrate with 0·01N-iodine with rotating platinum and satd. calomel electrodes. Results with a mean error of −3 to −3·5% were achieved. A new form of platinum electrode, which is rotated by means of a magnetic stirrer, is described. J. ZÝKA

3814. **Chromatography of dyestuffs intermediates. XII. Chromatographic separation and identification of the 2-naphtholsulphonic acids.** J. Latinák (Východočeské Chem. Závody-Synthesia, Pardubice-Semtín, Czechoslovakia). *Coll. Czech. Chem. Commun.*, 1961, **26** (2), 403–415 (in German).—All isomeric 2-napththol-mono-, -di- and -tri-sulphonic acids are separated by ascending paper chromatography. Solvents used are n-butanol - acetic acid - water (4:1:5) for the mono-acids and n-propanol - 5% aq. $NaHCO_3$ (2:1) for the poly-acids. The R_F values are tabulated. The spots are detected by u.v. fluorescence and by spraying with diazotised *p*-nitroaniline. The presence of 2-naphthol-3- and -5-sulphonic acids and -3,8- and -3,5-disulphonic acids in sulphonation mixtures is established, but no 2-naphthol-7-sulphonic acid and very little -1,7- or -3,7-disulphonic acid is present. J. P. STERN

3815. **Spectrofluorimetric determination of anthracene, fluorene and phenanthrene in mixtures.** G. A. Thommes and E. Leininger (Kedzie Chem. Lab., Michigan State Univ., E. Lansing, U.S.A.). *Talanta*, 1961, **7** (3–4), 181–186 (in English).—In fluorescence measurements on mixtures of anthracene (**I**), fluorene (**II**) and phenanthrene (**III**), only the fluorescence of **I** at 400 mμ is free from interference, and readings at 316 and 350 mμ are dependent on the concn. of all 3 compounds. By correcting for the emission of **I** at 316 and 350 mμ, mixtures of **I** with **II** or **III** can be resolved. Mixtures of **II** and **III** are resolved by using a calibration grid. The usually relative error is 5% for 0 to 5 p.p.m. P. D. PARR-RICHARD

3816. **Control of the sulphonation of anthraquinone by means of partition paper chromatography.** E. V. Sokolova (K. E. Voroshilov Sci. Res. Inst. of Org. Intermediates and Dyestuffs). *Zavod. Lab.*, 1961, **27** (2), 150–154.—Improvements in the method of Večeřa *et al.* (*Anal. Abstr.*, 1956, **3**, 1798) are described. G. S. SMITH

3817. **Analytical aspects of hydrogen exchange between hydrocarbons and sulphuric acid.** A. Y. Mottlau (Esso Res. and Engng Co., Linden, N.J., U.S.A.). *Anal. Chem.*, 1961, **33** (2), 293–297.—The rate of exchange of H between H_2SO_4 and different paraffins or naphthenes can be determined by shaking the sample for $\simeq$10 min. with ^{3}H-labelled H_2SO_4 and then analysing the treated hydrocarbon in a gas chromatograph connected to a proportional counter of the Wolfgang - Rowland type (*cf. Anal. Abstr.*, 1958, **5**, 3373). Applications of this radioassay procedure include identification of monomers and isomers in C_6 and C_7 paraffins, determination of saturates in unresolved chromatographic peaks, separation and identification of paraffins and naphthenes in oil fractions, and simplification of kinetic studies of carbonium-ion intermediates. W. J. BAKER

3818. **Hydrocarbon-group mass-spectrum analysis of petrols. II. Investigation of olefinic products.** G. Franke (B.P. Benzin u. Petrol. A.-G., Raffinerie Hamburg, Hamburg-Finkenwerder). *Erdöl u. Kohle*, 1960, **13** (11), 850–852.—The mass spectrum is recorded before and after treatment of the sample with benzenesulphinyl chloride, prepared by the chlorination of thiophenol. The reagent is added dropwise to the sample at 0°, the completion of the reaction being marked by the appearance of a yellow coloration. Any excess of reagent is removed by shaking the mixture with mercury, and centrifuging. This reaction converts the unsaturated components of the sample into compounds of high mol. wt., which do not contribute to the spectrum of the non-olefinic components; the olefinic content can then be calculated from the difference between the spectra. D. DEVOY

3819. **Improved chromatographic analysis of petroleum porphyrin aggregates and quantitative measurement by integral absorption.** W. W. Howe (Colorado Sch. of Mines Found., Inc., Golden, U.S.A.). *Anal. Chem.*, 1961, **33** (2), 255–260.—By using silica-gel columns, with $CHCl_3$ as the eluent, the porphyrin aggregates are separated into groups according to the spectral types. After further purification on activated alumina, with benzene as eluent, the individual fractions are analysed by an integral absorption method. Results from four petroleum samples are presented and discussed. G. P. COOK

3820. **Micro-determination of vanadium and nickel in crude oil and crude oil products.** G. E. Janauer and J. Korkisch (Anal. Inst., Univ. Wien,

Austria). *Z. anal. Chem.*, 1961, **179** (4), 241–245 (in German).—The sample (1 to 5 g) is digested with H_2SO_4 and HNO_3 until a clear soln. is obtained. The mixture is then evaporated to dryness, conc. HCl (10 ml) is added and the mixture is again evaporated. The residue is dissolved in 6N-HCl (10 ml), methanol (90 ml) is added and the soln. is passed through a Dowex-1 column at 0·5 ml per min. Before use the column is treated for 6 hr. with a mixture of 6N-HCl and methanol (1:9), and the test soln. is washed through the column with 5 ml of the same mixture. Iron, U, Cu, Mo, W and Co are retained on the column; V and Ni pass through and are determined spectrophotometrically with Solochrome fast gray (Fast grey RA) and Solochrome red ERS (C.I. Mordant Red 7), respectively. The method permits determination of metal contents of < 4 p.p.m. Dry-ashing caused low results. A. J. BENNETT

3821. **Polarographic method for parts per billion [U.S.] of copper and lead in catalytic reformer feedstocks.** B. W. Samuel and J. V. Brunnock (British Petroleum Co., Ltd., Sunbury-on-Thames, Middx., England). *Anal. Chem.*, 1961, **33** (2), 203–205.—From 10 to 100 parts per 10^9 of Pb and Cu can be determined simultaneously, in 10 ml of the pretreated sample soln., by recording the square-wave polarogram of an aliquot between $-0{\cdot}1$ and $-0{\cdot}6$ V applied d.c. potential against the mercury-pool anode. The concn. of each metal is obtained by referring the peak height to the working graph. The results agree with those for the usual colorimetric methods, and the precision is $\simeq 2$ and $\simeq 3$ parts per 10^9 for Pb and Cu, respectively (duplicate determinations). The chief merit of the method is its accuracy for measuring concn. of < 20 parts per 10^9. Pre-treatment of the sample (100 ml) consists in oxidation with Br in CCl_4, extraction into warm 4N-HCl, concentration of the extract and destruction of organic matter with HNO_3 - $HClO_4$, dissolution of the dry residue in 4N-HCl, and dilution to 10 ml with H_2O. The complete procedure takes $\simeq 4$ hr., of which only 2 hr. is manipulative time. Precautions must be taken against contamination by reagents and glassware.
W. J. BAKER

3822. **Determination of undissolved water in [oil] fuels.** L. Gardner and G. Topol (Fuels and Lubricants Lab., Nat. Res. Council, Ottawa, Canada). *Mater. Res. & Stand.*, 1961, **1** (2), 112–115.—From 2 to 100 p.p.m. of 'free' H_2O in jet fuel can be determined to within ± 2 p.p.m.by passing a known vol. (5 to 20 litres) of fuel from the effluent stream through a vertical column (3 in. × 1·5 in.) of resin-impregnated glass-fabric rings at the same temp. as the stream and positioned in a 2-litre flask. The rings are then allowed to fall to the bottom of the flask, the fuel therein is decanted until only $\simeq 250$ ml remains, and the H_2O absorbed by the fibrous glass is measured by distillation with xylene (750 ml), either immediately or later. A blank must be run for each test. The method, which is claimed to have advantages over the Karl Fischer procedures, is of particular use in evaluating filter-separators used during jet-fuel transfer and refuelling (residual H_2O in the effluent stream is a measure of filter efficiency). W. J. BAKER

3823. **Determination of traces of aromatic hydrocarbons in coal gas.** J. Novák (Lab. Anal. of Gases, Acad. Sci., Brno, Czechoslovakia). *Paliva*, 1961, **41** (3), 84–87.—The gas-chromatographic method with flame-ionisation detection and CHROM I apparatus was used. The adsorption column was packed with Celite 545 with 30% of squalane or Sterchamol with 25% of polyoxyethylene glycol. Nitrogen was used as the carrier gas. Benzene and its homologues (0·1 g per cu. metre of sample) were determined within 15 min., with a relative error of $\pm 5\%$. J. ZÝKA

3824. **Potentialities of capillary columns in the analysis of coal-tar fractions.** D. W. Grant (Coal Tar Res. Ass.). C.T.R.A. Report No. 0267, 1960.—High orders of resolution have been obtained on a capillary column having an efficiency of 500,000 theoretical plates and rapid analysis is shown to be possible on shorter columns. The limitations of the method are discussed. Factors which effect the accuracy of analysis include the linearity of the detector, the accuracy of sampling and the constancy of column conditions. The difficulty of obtaining accuracy of sampling makes accurate quantitative analysis impossible at present. The problem is illustrated by reference to the separation of anthracene and phenanthrene. Eight chromatograms given show the separation of the components of a crude anthracene oil, phenolic isomers, high-boiling compounds, etc.
FUEL ABSTR. AND CURR. TITLES

3825. **Use of four-electrode conductimetry for the automatic determination of carbon dioxide and ammonia in concentrated scrubbing water of coke-oven gas.** E. Barendrecht and N. G. L. M. Janssen (Centr. Lab. der Staatsmijnen in Limburg, Geleen, Holland). *Anal. Chem.*, 1961, **33** (2), 199–203.—A specially constructed cell is described, the use of which makes the determination independent of the flow rate of the scrubbing water through the cell. Under laboratory conditions, concn. of CO_2 and NH_3 of 20 to 40 g per litre can be determined with an accuracy within 0·5%; under industrial plant conditions the accuracy is $\simeq 3\%$ because of the presence of small and variable amounts of substances with an electrolytic nature. Carbon monoxide and oxygen do not interfere.
C. B. BAINES

3826. **Detection of terpinyl acetate in volatile oils.** D. van Os and F. H. L. van Os (Lab. f. Pharmakog. u. galen. Pharm., Univ. Groningen, Netherlands). *Pharm. Acta Helv.*, 1961, **36** (1–2–3), 170–175 (in German).—*Procedure*—Mix the sample of H_2O-free oil (2 g) with ethanol (20 ml) and heat under reflux for 1 hr. with 0·5N-ethanolic KOH; cool rapidly, titrate with 0·5N-HCl, with phenolphthalein as indicator, and calculate the saponification value. Similarly determine the saponification value without the addition of ethanol and with heating for 2 hr. instead of 1 hr. If the sample contains $> 2{\cdot}5\%$ of terpinyl acetate, the difference between the two values will exceed 1·5%. A. R. ROGERS

3827. **Contribution to the testing and standardisation of peppermint oil by thin-layer chromatography.** R. Jaspersen-Schib (Pharm. Inst., Eidg. Tech. Hochsch., Zürich). *Pharm. Acta Helv.*, 1961, **36** (1–2–3), 141–152 (in German).—The main constituents of oil of *Mentha piperita* can be separated and identified by thin-layer chromatography on a mixture of Kieselgel G and $CaSO_4$, with a 5% soln. of ethyl acetate in benzene as solvent. The chromatogram is examined in visible and u.v. light after development of the colour with a 1% soln. of

vanillin in conc. H_2SO_4. Adulteration with oil from other *Mentha* species or with entirely different oils, such as sandalwood, is easily detected.

A. R. ROGERS

3828. **Polarography of basic dyes.** J. Thurel and B. Drevon (Pharm. Chem. Lab., Fac. of Med. and Pharm., Univ., Lyons). *Ann. Falsif.*, 1961, **54**, 12–16.—Three synthetic basic dyes, forbidden for use in food in France, Auramine O (C.I. Basic Yellow 2), methyl violet and malachite green, can be detected in suitable mixtures of all three by polarography of a soln. in methanol (0·1 ml) of 50 to 100 μg of dye mixed with K H phthalate buffer (pH 5) (5 ml) at 25° ± 0·2°. The wave heights of methyl violet and malachite green are proportional to the concn. and they can be determined in methanol (5 ml) containing 20 to 100 μg in the same buffer with errors varying from −7·5 to + 8%. A maximum suppressor is not essential, but dissolved oxygen must be removed. The relative values for $E_{\frac{1}{2}}$ are Auramine O, − 1·03 V; methyl violet, − 0·83 V; and malachite green, − 0·72 V.

R. CLARKE

3829. **Extraction of acid dyes by quaternary ammonium bases.** J. Vollaire-Salva. *Ann. Falsif.*, 1961, **54**, 17–20.—Drevon and Laur's method (*Anal. Abstr.*, 1959, **6**, 4962) is modified. *Procedure for confectionery products*—Remove the colloids from a 20% (w/v) aq. soln. (1 vol.) by adding 95% ethanol or acetone (2 vol.), filter, remove the solvent by distillation under reduced pressure, and restore to the original concn. Adjust 25 ml to pH 9 with 10% Na_2CO_3 soln., add 0·1% cyclohexylhexadecyldimethylammonium bromide (10 ml) and extract with $CHCl_3$ (2 × 10 ml). Wash the $CHCl_3$ layer with water (2 × 20 ml), extract the dye from the combined $CHCl_3$ layers with 1-ml portions of HCl (3 to 5 ml), and evaporate to dryness under reduced pressure. Re-dissolve the dye in aq. NH_3 (1:4) and chromatograph by the ascending technique with S. & S. paper 2043b Mgl.

R. CLARKE

3830. **A simple dyeing test to distinguish between Courtelle, Orlon Type 42 and Standard Acrilan.** K. Meldrum. *J. Soc. Dy. Col.*, 1961, **77** (1), 22.—The test involves the use of Sevron Orange L in the presence of sulphuric acid together with a level-dyeing acid dye (*e.g.*, Lissamine Green SFS) (C.I. Acid Green 7) and a non-ionic anti-precipitant (*e.g.*, Lubrol W). The fibre is treated while boiling for 15 min.: Orlon Type 42 stains red, Standard Acrilan green and Courtelle pale orange.

SHIRLEY INST. ABSTR.

3831. **Determination of starch in wood.** F. R. Humphreys and J. Kelly (Div. of Wood Technol., Forestry Commission of N.S.W., Sydney, Australia). *Anal. Chim. Acta*, 1961, **24** (1), 66–70 (in English).—Ground wood is digested in $HClO_4$ to disperse the starch and, after centrifuging, an aliquot is neutralised and treated with acetic acid, KI and KIO_3 soln. The colour is allowed to develop and the extinction is measured at 650 mμ. The standard reference curve was prepared with potato starch. A correction factor is given to allow for the different amylose contents of the two starches.

A. C. R. HARTLEY

3832. **Use of carboxylic acid cation-exchange resin in the analysis of copper in chromated wood-preservative solutions.** R. A. Edge (Univ. of Cape Town, Rondebosch, S. Africa). *Anal. Chim. Acta*, 1961, **24** (2), 143–145 (in English).—The preservative soln. contain $CuSO_4$ and $Na_2Cr_2O_7$. Sodium arsenate or borate may also be present. *Procedure*—To an aliquot containing 0·2 to 0·6 milli-equiv. of Cu add 5N-aq. NH_3 in slight excess and pass the soln., and 10 ml of rinse water, through a column containing 20 to 30 g of Amberlite IRC-50 resin (0·3 to 0·5-mm mesh) (NH_4^+ form) at a flow rate of 0·25 ml per min. Wash the column with 20 ml of water. Elute with 20 ml of 2N-HCl and titrate the Cu^{2+} in the eluate by the iodimetric method.

H. N. S.

3833. **Improvements in the acidolysis procedure for lignin isolation and in the procedure for the analysis of lignin oxidation products.** J. M. Pepper and M. Siddiqueullah (Univ. Saskatchewan, Saskatoon, Canada). *Canad. J. Chem.*, 1961, **39** (2), 390–391.—*Acidolysis procedure*—The acid extract is concentrated under reduced pressure and lignin is pptd. by adding the extract to a large excess of vigorously stirred water. The lignin coagulum settles rapidly, a clear mother-liquor remains, and there is little colloidal loss during subsequent washing with water. *Analysis of the alkaline nitrobenzene oxidation products*—The method of Stone and Blundell (*Brit. Abstr. C*, 1951, 339) is modified to produce homogeneous samples for chromatography. The alkaline reaction product is continuously extracted with ether to remove nitrobenzene and its reduction products, and is then acidified. Further ether extraction removes the lignin oxidation products, which are then brought into ethanolic soln. suitable for chromatography by solvent exchange. The chromatographic papers should be equilibrated over water in a closed vessel for at least 2 days before use, and this equilibrium should be carefully maintained during loading of the paper.

A. C. R. HARTLEY

3834. **Quantitative chemical analysis of binary mixtures of cellulose triacetate and certain other fibres.** British Standards Institution (2 Park Street, London, W.1). B.S. 3344:1961. 9 pp.—A method based on the solubility of cellulose triacetate in dichloromethane is described.

3835. **Xanthate sulphur determination [in viscose] by the batch ion-exchange method.** L. H. Phifer and J. L. Bell (American Viscose Corp., Marcus Hook, Pa.). *TAPPI*, 1960, **43** (7), 622–626.—Approx. 2 g of viscose is dispersed in 250 ml of 0·1% NaOH soln. Aliquots of 5 ml in 125-ml flasks were diluted to 50 ml with NaOH soln. to give a NaOH concn. of 0·4 to 8·0%. Excess of Amberlite resins IRA-400 or IRA-410 was added to various samples and the extinctions of the filtrates were measured at 303 mμ. The absorptivity of xanthate was taken as 15,900. Resin IRA-400 was better than IRA-410, especially at higher alkalinities. The results of this method are more precise than and in good agreement with those of other methods.

R. AICHER

3836. **Cleanliness of fillings and stuffings for bedding, upholstery, toys and other domestic articles.** British Standards Institution (2 Park Street, London, W.1). Amendment No. 1 (20.2.61) to B.S. 1425:1960. 4 pp.—Numerous amendments are listed and a summary of cleanliness test requirements is given in the form of a table.

3837. **Determination of ethylene - propylene copolymer composition by infra-red analysis.** P. E. Wei (Chem. Res. Div., Esso Res. and Engng Co., Linden, N.J., U.S.A.). *Anal. Chem.*, 1961, **33** (2), 215–217.—The method is based on the measurement of the absorption intensities at 13·9 and 8·7 μ of solid copolymer films. The ratio of the intensities is directly proportional to the ratio of the ethylene and propylene units present. G. P. Cook

3838. **Spectrographic determination of ethylbenzene impurity in styrene.** A. L. Gol'denberg and A. E. Semenova. *Plast. Massy*, 1960, (3), 63–65; *Ref. Zhur., Khim.*, 1960, (23), Abstr. No. 92,116.—An i.r. spectrometer IKS-11 with a lithium fluoride prism is used for the spectrographic determination of small amounts (0·3 to 0·8%) of ethylbenzene (**I**) in styrene (**II**), with a slit-width of 0·145 mm and a layer of **II** >0·5 mm thick. The band used is the absorption band at 2873 cm^{-1}, characteristic of the valency vibrations of methyl groups; **II** free from **I** is used as standard. Beer's law is obeyed for concn. of **I** from 0·1 to 1%. The mol. extinction coeff. is 27. The mean error is 5 to 7% at a sensitivity of 0·1%. C. D. Kopkin

3839. **Spectroscopic determination of ethylbenzene in industrial styrene.** A. N. Shabadash and N. F. Kharitonova. *Plast. Massy*, 1960, (3), 65; *Ref. Zhur., Khim.*, 1960, (23), Abstr. No. 92,117.—A modified procedure is proposed for the spectrographic determination of ethylbenzene (**I**) in styrene (**II**) (*cf.* Gol'denberg and Semenova, *Anal. Abstr.*, 1961, **8**, 3838), which eliminates the disadvantage that the pure **II** used as standard polymerises on storage. The optical density (D) of **I** is found from the formula $D = \log I_0/I_{anal.}$, where I_0 is the intensity of the light after absorption by the sample at 2782 cm^{-1} (where only **II** absorbs), and $I_{anal.}$ is the intensity at 2873 cm^{-1}. The need for a standard is removed, and errors due to the presence of impurities (xylenes, isopropylbenzene, etc.) in **II** are eliminated. The sensitivity of the method increases with decreasing **I** concn.; the relative error at concn. of **I** from 0·25 to 3·00% is within the range ±15%. C. D. Kopkin

3840. **Determination of small amounts of caprolactam in aqueous solutions.** K. E. Istomina and L. A. Ionova (State Inst. of the Nitrate Ind.). *Zavod. Lab.*, 1961, **27** (2), 160–162.—A method based on that of Bergman (*Brit. Abstr. C*, 1953, 12) is described. The sample (50 ml) containing caprolactam is neutralised with 0·1N-acid or -alkali and boiled for 30 min. under reflux with 30 ml of 3M-hydroxyammonium chloride and 5 ml of N-NaOH. The cooled soln. is treated with 2·5 ml of 2N-HCl and 15 ml of 10% $FeCl_3$ soln. and diluted to 100 ml. After 10 min. the extinction is measured at 500 mμ. G. S. Smith

3841. **Analysis of a mixture of solvents [for lacquer] by infra-red spectrometry.** F. Lalau-Keraly. *Peint.-Pigm.-Vern.*, 1961, **37** (1), 4–8.—The procedure for analysis of a typical lacquer solvent mixture containing ethyl methyl ketone, methanol, trichloroethylene, butanol and butyl acetate is described. A qualitative analysis is first carried out by separating the mixture into 11 fractions by distillation, and examining the i.r. spectrum of each fraction. The composition is then determined quant. by measuring the extinctions at various wavelengths and solving the series of equations obtained. A final adjustment may be necessary by comparison of the spectrum of the solvent mixture with that of one made up to the estimated composition. L. A. O'Neill

3842. **Identification of elastomers.** A. Garcia Vargas. *Rev. Plasticos, Madrid*, 1960, **11**, 409–414.—The following series of tests is proposed and the behaviour of the main types of rubber shown in tabular form—heating in a flame; examination of fluorescence under ultra-violet light; measurement of brittle-point on cooling; pyrolysis and testing of the vapours with various indicator soln. and papers. Specific tests are given for polymers of chloroprene, vinyl acetate, isobutylene, styrene and natural rubber. L. A. O'Neill

3843. **Methods of testing rubber latex. Part 2: Chemical and physical tests.** British Standards Institution (2 Park Street, London, W.1). B.S. 1672: Part 2: 1954. Amendment No. 3 (27.4.61). 4 pp.—A number of new sections and amendments are included.

3844. **Determination of traces of copper in rubber-latex ash by neutron-activation analysis.** J. A. W. Dalziel and R. C. H. Hsia (Dept. of Chem., Imperial Coll. of Sci. and Technol., London, S.W.7). *J. Sci. Food Agric.*, 1961, **12** (2), 127–130.—Neutron activation causes the reaction $^{63}Cu\ (n\gamma)^{64}Cu$, which decays with $t_{\frac{1}{2}} = 12{\cdot}5$ hr. End-window counting may be used for measuring the β-activity of solid material and liquid-scintillation techniques may be used to measure γ-activity. The end-window method is twice as sensitive as the scintillation method, but the scintillation method is simpler, since it requires only pptn. as sulphide to eliminate interfering activities, whereas the end-window method needs further purification by electro-deposition. The main interference is from ^{32}P. A typical sample of ash contained 370 ± 20 p.p.m. of Cu. J. R. Hudson

3845. **Rapid determination of zinc, calcium and magnesium in vulcanised rubber by chelatometric titration.** Fumio Fujita, Hideo Matsushita and Hiroshi Omori (Res. Inst., Toyo Rubber Ind., Amagasaki, Hyogo-ken). *J. Soc. Rubber Ind., Japan*, 1960, **33** (9), 661–668.—*Procedure*—Ignite the sample (1 to 2 g) below 550°, dissolve the residue in HCl (5N, 30 ml), filter off the Si, Ba, Ti and Pb, boil with HNO_3, and remove Fe and Al with aq. NH_3. Make the filtrate 2N in HCl, pass it through a column of Amberlite IRA-140 (Cl^- form) and titrate the Ca and Mg in the percolate with EDTA (disodium salt). Elute the Zn from the column with 0·1N-HNO_3 and titrate it with EDTA (disodium salt). K. Saito

3846. **Titrimetric determination of hexahydro-1,3,5-trinitro-sym.-triazine (RDX) and octahydro-1,3,5,7-tetranitro-sym.-tetrazine (HMX) with ferrous sulphate.** J. Šimeček (Military Acad. A. Zápotocký, Brno, Czechoslovakia). *Anal. Chem.*, 1961, **33** (2), 260–262.—The HNO_3 formed when RDX and HMX (< 0·005 mole) are dissolved in conc. H_2SO_4 is measured by titrating the soln. potentiometrically with Fe^{3+} soln. G. P. Cook

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See also Abstracts—**3560**: *Section II*, Se in nicotinic acid. *Section IV*, Organic analysis. **3561**: *Section Vb*, Polarography of *N*-2,3-dimercaptopropyl)phthalamic acid. Separation of

nitropropane and nitrobutane. *Section VI*, Gas chromatography of higher alcohols and paraffins. Paper chromatography of di- and tri-hydric phenols. Starch hydrolysis. Poly(alkyl methacrylates). Fatty acids in lubricating grease and soap. *Section VIIa*, Spectrophotometry of pinacyanol and pinakryptol green. **3569**, Purification of dimethylformamide. **3572**, Analysis of gas mixtures. **3640**, C in org. compounds. **3656**, Analysis of Pb tannate. **3862**, Paper chromatography of sugar phosphates. **3930–3933**, Dyes for use in foods. **3956**, Chlorinated aliphatic hydrocarbons in air. **3985**, Apparatus for Kjeldahl method. **3989**, Chromatographic reagents for nitrogenated compounds and carbohydrates. **3994**, Gas chromatography of polyphenyls. **3998**, Flame ionisation chromatography of hydrocarbon mixtures. **4023**, Titration of acids and bases with metal - metal oxide electrodes.

4.—BIOCHEMISTRY

INCLUDING DRUGS, FOOD, SANITATION, AGRICULTURE

Biological fluids, animal and vegetable tissues

3847. **Simple method of estimating the tritium content of biological samples.** G. G. Steel (Phys. Dept., Inst. of Cancer Res., Belmont, Surrey, England). *Int. J. Appl. Radiation and Isotopes*, 1960, **9** (1–4), 94–99.—The sample, mixed with CuO, is heated in a tube that also contains a layer of heated CuO through which the H_2O produced is passed; a layer of a mixture of glucose and CuO is heated after the combustion of the sample and the H_2O produced assists the transfer of the tritiated H_2O to the other end of the tube, which is kept at −65°. The tritiated H_2O is then added, with ethanol, to the liquid scintillator and the activity is measured with a counter having an efficiency of 10% and a background of 10 counts per sec.; a standard addition of ^3H is then made and the activity is recorded again. The recovery of ^3H is >95%. The time required for a determination is 30 min. G. J. HUNTER

3848. **Rapid assay procedures for tritium-labelled water in body fluids.** B. E. Vaughan and E. A. Boling (U.S. Naval Radiological Defense Lab., San Francisco, Calif., U.S.A.). *J. Lab. Clin. Med.*, 1961, **57** (1), 159–164.—In the first method described, the sample (0·5 to 2 ml) is vacuum-sublimed in a special small glass flask to eliminate errors due to light-quenching substances in the sample. The melted sublimate is then diluted with a scintillation liquid for counting. When a larger sample is available, or sublimation is impracticable, an alternative method requiring internal standardisation with tritiated water may be employed; this gives slightly less accurate results and necessitates a separate water determination on the sample. The application of the methods for determining total body water, and the results obtained, are discussed.
W. H. C. SHAW

3849. **Determination of fall-out caesium-137 in animal and plant tissues.** C. Blincoe (Dept. Agric. Chem., Univ. Nevada, Reno, U.S.A.). *J. Agric. Food Chem.*, 1961, **9** (2), 127–129.—The residue obtained from the sample by dry-ashing at 550° and several subsequent treatments with HNO_3 and ignitions at 550° is moistened with $HClO_4$ and heated at 550° to expel Ru. The sol. matter of the final ash is quant. extracted with HCl; to the acid soln. (25 to 35 ml, containing the equiv. of 4 ml of conc. HCl) are added CsCl (10 mg, as carrier), 0·2M-$Co(NO_3)_2$ (2 ml) and finally, after heating at 100° for 5 min., 0·2M-$K_3Co(CN)_6$ (2 ml). The ppt is separated by centrifuging, and the ^{137}Cs co-pptd. with the cobaltous cobalticyanide is determined with a well-type scintillation counter, a single-channel pulse-height analyser and a scaler. If required, the ^{90}Sr can be pptd. (with a carrier) as carbonate from the supernatant liquid or from the HCl soln. of the ash before the co-pptn. of the ^{137}Cs. The method is suitable for routine analyses. Recoveries of Cs, with ^{134}Cs as tracer, from liver or muscle tissue are ≃99%. P. S. ARUP

3850. **Determination of calcium in biological material. The use of calcein as an indicator in the EDTA titration.** T. Y. Toribara and L. Koval (Dept. of Rad. Biol., Univ. of Rochester, New York, U.S.A.). *Talanta*, 1961, **7** (3–4), 248–252 (in English).—*Procedure*—Dilute 0·5 ml of serum with H_2O (4 ml), add 4 drops of acetic acid, 1 drop of bromocresol green indicator, 4% ammonium oxalate soln. (1 ml) and conc. aq. NH_3 soln. to give a pH of 4·7 (blue - green). Cool overnight, centrifuge, and decant the liquid. Dry and heat the pptd. Ca oxalate in the tube at 500° for 1 hr. Cool, add 1 drop of HCl (1:3), 5 ml of H_2O, 1 ml of 4% KOH soln. and 0·05 ml of calcein soln. (0·004% in 0·25N-KOH). Titrate with 0·0005M-EDTA (disodium salt) under u.v. light.
P. D. PARR-RICHARD

3851. **Calcium and magnesium determination in bovine blood by EDTA titration.** G. M. Ward, R. C. Lindsay and C. A. Vair (Colorado State Univ., Fort Collins, U.S.A.). *J. Dairy Sci.*, 1960, **43** (7), 1014–1015.—The determinations may be carried out simply and rapidly by titration of the blood-serum samples with EDTA, with Cal-Red as indicator at pH 12 for Ca^{2+} and Eriochrome black T as indicator in aq. NH_3 buffer (pH 10·2), and in the presence of sodium tungstate, for Mg^{2+}. The correlation of results with those obtained by standard methods is given and discussed.
W. H. C. SHAW

3852. **Estimation of calcium and magnesium in blood serum by the cathode-ray polarograph.** E. A. Irving and P. S. Watts (Inst. of Med. and Vet. Sci., Adelaide, S. Australia). *Biochem. J.*, 1961, **79** (2), 429–432.—The sum of Ca and Mg is determined first and then the Mg alone is determined after pptn. of the Ca as oxalate; Ca is obtained by difference. The method is as accurate as, and more rapid than, available chemical methods. The results for Ca tend to be slightly higher than those obtained by chemical methods. J. N. ASHLEY

3853. **Rapid and sensitive sub-micro phosphorus determination.** C. J. F. Böttcher, C. M. van Gent and C. Pries (Leiden Univ., Netherlands). *Anal. Chim. Acta*, 1961, **24** (2), 203–204 (in English).—In the method of Bartlett (*Anal. Abstr.*, 1959, **6**, 4895) the initial digestion of the organic material with H_2SO_4 requires 4·5 hr. The digestion time is reduced to 40 min. if the sample is heated with 70% $HClO_4$ (0·2 ml) in a tube (125 mm × 15 mm) standing to a depth of 30 mm in a thermostatically controlled heating block at 180°. The liquid clears after 12 to 18 min. and is heated for a further 20 min. H. N. S.

3854. **Determination of inorganic sulphate in studies on the enzymic and non-enzymic hydrolysis of carbohydrate and other sulphate esters.** K. S. Dodgson (Dept. of Biochem., Univ. of Wales, Cardiff). *Biochem J.*, 1961, **78** (2), 312–319.—Three modifications of a turbidimetric method, differing essentially only in the scale of working, are described. The SO_4^{2-} are pptd. as $BaSO_4$ with a 0·5% aq. soln. of $BaCl_2$ containing 0·5% of gelatin, which acts as a stabiliser. The suspension is stable for at least 1 hr. and the extinction is measured in a quartz cell at 360 mμ. It can also be measured at 500 mμ (but with less sensitivity) when materials which tend to absorb u.v. light are present. The methods are simple and rapid, but are less sensitive than the benzidine or chloranilate methods. The first modification is used for the range 0 to 200 μg of SO_4^{2-} and is suitable for following the non-enzymic hydrolysis of monosaccharide sulphates by hydrazine; the second modification, which is applicable to the determination of up to 40 μg of SO_4^{2-}, is used for the assay of purified glycosulphatase preparations; the third method, which covers the range 0 to 12 μg of SO_4^{2-}, is used for the micro-analysis of various ester sulphates. The modifications can be used in the presence of hydrazine, imidazole, various buffers, anions and cations, monosaccharide mono- and di-sulphates, and some sulphate esters, but SO_3^{2-}, Ba^{2+} and $P_2O_7^{4-}$ (in concn. > 0·01M) and many polysaccharide sulphate esters interfere. J. N. ASHLEY

3855. **Radiochemical investigation of the behaviour of inorganic ions in gel filtration with Sephadex. Micro-determination of protein-bound iodine in blood serum.** H. Spitzy, H. Skrube and K. Müller (Chem. Abt., Paracelsus Inst., Bad Hall, Austria). *Mikrochim. Acta*, 1961, (2), 296–307 (in German).—Inorganic ions may be rapidly removed from protein soln. by gel filtration with a dextran gel, Sephadex (*cf.* Porath and Flodin, *Nature*, 1959, **183**, 1657). The behaviour of the ions depends on their concn., on the soln. used to swell the Sephadex and on the soln. used as eluent. In soln. of low ionic strength, cations are adsorbed but anions are not. On increasing the ionic strength of the eluent, both cations and anions are adsorbed by the gel, and it is possible to separate inorganic ions from proteins. For the removal of I^- from serum samples before the determination of protein-bound iodine, the sample (0·5 ml) is applied to a column (120 mm × 10 mm) of Sephadex treated with 0·9% NaCl soln. and eluted with 0·9% NaCl soln. at 0·75 ml per min.; 1-ml fractions of eluate are collected. Protein is removed quantitatively in fractions 3 to 7 and I^- in fractions 9 to 14. Twelve comparison analyses of samples containing 2 to 13 μg of protein-bound iodine per 100 ml by the gel-filtration and trichloroacetic acid pptn. methods gave results agreeing to within 5%. The gel-filtration method is particularly suitable for the analysis of serum samples containing abnormally large amounts of I^-. W. T. CARTER

3856. **Micro-determination of iron in biological material with ferron.** V. Kauppinen (Dept. Biochem., Univ. Helsinki, Finland). *Suomen Kem. B*, 1961, **34**, (2), 27–29 (in English).—The method is based on the procedure of Ziegler *et al.* (*Anal. Abstr.*, 1957, **4**, 2978). In six experiments, the recovery of Fe from samples of yeast ranged from 99·5% to 103%. *Procedure*—Digest the sample (*e.g.*, 100 mg of dry yeast containing 1 to 7 μg of Fe) with conc. H_2SO_4 (1 ml) and 30% H_2O_2 soln. until clear; heat for ≮45 min. until decomposition of H_2O_2 is complete; cool, add H_2O (5 ml) and heat at 90° for ≮30 min. to decompose pyrophosphates; cool, dilute with H_2O to 5 ml and add 0·025% ferron soln. (2 ml). Treat a reagent blank and standard Fe soln. similarly. Neutralise the reagent blank with aq. NH_3 to the yellow - green colour of ferron and add the same vol. of aq. NH_3 to the other soln. Then add acetate buffer soln. (pH 4·6) (2 ml) and tri-n-butylammonium acetate (0·1 ml), extract with $CHCl_3$ (3 × 0·5 ml), dilute the combined extracts with $CHCl_3$ to 2·5 ml and measure the extinction at 610 mμ. A. R. ROGERS

3857. **Determination of iron-55 and -59 in blood.** L. Hallberg and H. Brise (Dept. of Med., Univ. Göteborg, Sweden). *Int. J. Appl. Radiation and Isotopes*, 1960, **9** (1–4), 100–108.—The preparation of sources by electro-deposition is considered in detail. The sample, after preliminary treatment, is digested with H_2SO_4 and then with $HClO_4$. After the pptn. of $Fe(OH)_3$ it is dissolved in 6N-H_2SO_4, and 50% $(NH_4)_2SO_4$ soln. (2 ml) and satd. ammonium oxalate soln. (35 ml) are added. The Fe is then deposited on a copper planchette by passing a current of 0·4 amp. for 4 hr., with a platinum spiral anode at a distance of 2 cm. The planchette is washed with ethanol and counted in a gas-flow counter, first with a 0·75-mm beryllium absorber and then with a 0·011-mm platinum absorber, and the contributions from ^{55}Fe and ^{59}Fe are calculated. The recovery of Fe is ≃95%. G. J. HUNTER

3858. **Simultaneous determination of ethyl ether and ethanol in blood and viscera by gas chromatography. Application to a medico-legal case.** L. Maricq and L. Molle (Lab. de Chim. Toxic., Univ. Libre de Bruxelles, Belgium). *Ann. Pharm. Franç.*, 1960, **18** (11), 811–816.—After suitable preparation, samples from blood and viscera are chromatographed on Carbowax 1500 on Celite in a 4-metre column at 106° ± 0·5°, with H as carrier gas at 25 ml per min. *Procedure*—For blood, 5 ml is pptd. with tungstophosphoric acid and, after centrifugation, 10 μl of the supernatant liquid is injected into the gas stream. For brain, 150 g of the organ is distilled with 100 ml of satd. aq. picric acid, and 50 ml is collected. This vol. is reduced to 10 ml by fractional distillation and 10 μl is injected on to the column. For stomach contents, a procedure similar to that for brain is described. E. J. H. BIRCH

3859. **Colorimetric determination of meprobamate.** O. D. Madsen and V. Schmidt (Centrallab., Centralsygehuset, Nyköbing, Denmark). *Ugeskr. Laeg.*, 1960, **122** (26), 891–893.—The colorimetric method of Hoffman and Ludwig (*Anal. Abstr.*, 1960, **7**, 3402) was used for the determination of meprobamate in serum or plasma, and was found to be satisfactory for clinical use, with an accuracy of 5 to 10%. The prescribed procedure must be strictly adhered to. P. PEDERSEN

3860. **Improved photometric method for assaying phenolsulphonephthalein in the blood of cattle in tests for renal function.** R. R. Anderson and J. P. Mixner (New Jersey Agric. Expt. Sta., Sussex, U.S.A.). *J. Dairy Sci.*, 1960, **43** (10), 1471–1475.—Errors due to free haemoglobin (**I**) in plasma samples containing phenolsulphonephthalein (**II**) are minimised by the procedure described. From a study of the extinction of samples without **II**,

but with varying degrees of induced haemolysis, a regression equation is derived from which the correction required for **I** under the basic conditions used for the photometric measurement of **II** may be calculated from the extinction in acid solution. The accuracy and precision of the method are discussed. W. H. C. SHAW

3861. **Correction for haemolysis in a photometric method for assaying sulphobromophthalein in the blood of cattle in tests for hepatic function.** R. R. Anderson and J. P. Mixner (New Jersey Agric. Expt. Sta., Sussex, U.S.A.). *J. Dairy Sci.*, 1960, **43** (10), 1465–1470.—Errors due to free haemoglobin (**I**) in plasma samples containing sulphobromophthalein (**II**) are minimised by the procedure described. From a study of the extinction of samples without **II**, but with varying degrees of induced haemolysis, a regression equation is derived from which the correction required for **I** under the basic conditions used for the photometric measurement of **II** may be calculated from the extinction in acid solution. Improved precision and accuracy are attained, but the method should be applied only when haemolysed plasma samples are to be assayed. W. H. C. SHAW

3862. **Two-dimensional system of paper chromatography of some sugar phosphates.** E. J. Wawszkiewicz (Dept. of Biochem., Univ. Calif., Berkeley, U.S.A.). *Anal. Chem.*, 1961, **33** (2), 252–254.—To prevent trailing of the phosphate esters, EDTA (ammonium salt) (pH 5) is added to each of the two solvents [7·7% ammonium acetate soln. (pH 5) - 95% ethanol (3:7), and 95% ethanol - n-butanol (32:52·5) to which is added 2 g of picric acid], and paper washed with 1% oxalic acid soln. is used. R_F data for 40 compounds are listed. G. P. COOK

3863. **Densitometric determination of aesculin and fraxin after paper electrophoresis.** G. Faugeras and R. Paris (Lab. de Mat. Méd., Fac. de Pharm., Paris). *Ann. Pharm. Franç.*, 1960, **18** (10), 698–704. —The optimum conditions for the separation of aesculin or fraxin from possible interfering substances and their subsequent determination were investigated and the following method was developed. *Procedure*—A sample of 10 µl containing 5 to 10 µg of aesculin or fraxin is placed on Arches 302 paper soaked in 0·5% sodium borate soln. Equal vol. of at least four different standard soln., with a content of pure substance between 1 and 10 µg, are also placed on the paper and the electropherogram is run for 2 to 3 hr. at 10 to 20 V per cm. The extinction of the dried strip is then determined at 365 mµ. The densitometer is first used in the direction of the electrophoresis to ensure perfect separation of the aesculin or fraxin, and then mm by mm across the strip at the level of the subject and control spots. The sums of the extinctions give a calibration curve from which the concn. in the subject spot is determined. When the spot is not sufficiently isolated, the determination is possible by constructing a curve of the variation of extinction in the spot and extrapolating when necessary, and determining the area of the peak with a planimeter. E. J. H. BIRCH

3864. **Examination of an infra-red method for determination of ratio of coproporphyrin isomers I and III.** H. L. Dinsmore and C. J. Watson (Minnesota Univ., Minneapolis, U.S.A.). *J. Lab. Clin. Med.*, 1960, **56** (4), 652–658.—The method depends on the differences in infra-red spectra (8 to 9 µ) of the solid methyl esters of coproporphyrins I and III. The proportions are calculated by a difference technique, but uncontrollable variation in the ratio of crystalline to amorphous material limits the accuracy to ≃15%. The method is inferior to fluorescence and chromatographic procedures, but is useful as an independent check and for identifications. W. H. C. SHAW

3865. **Resolution of phosphatides by chromatography on a thin film of silica gel.** W. Schlemmer (Ist. di Chim. Biol., Univ. Bologna, Italy). *Boll. Soc. Ital. Biol. Sper.*, 1961, **37** (3), 134–137.—A rapid method is briefly described. A silica-gel film (≃250 µ thick) is prepared on a sheet of glass (20 cm × 20 cm) by means of a special apparatus (Desaga, Heidelberg) and heated for 1·5 hr. at 120° before use. Successful separations of up to 250 µg of mixed phosphatides were achieved with $CHCl_3$ - methanol - water (75:22:3 or 13:6:1) as solvent. Individual phosphatides were detected by spraying with ammonium molybdate soln. (3 g in 250 ml of water plus 30 ml of N-HCl plus 15 ml of 60% $HClO_4$) and heating at 105° for 20 min. The R_F values decrease in the order neutral fats, cholesterol, free fatty acids, cardiolipin (and similar compounds), cephalin, lecithin, lysocephalin, sphingomyelin, lysolecithin and aminoacids. The sensitivity limit is from 2 to 5 µg. The method is rapid (35 min. for a 10-cm run) and is suitable for the identification of lipid mixtures or of phospatides in column eluates. E. C. APLING

3866. **Simple spectrophotometric method for the determination of urea in blood and urine.** T. K. With, T. D. Petersen and B. Petersen (Central Lab., Svendborg County Hosp., Denmark). *J. Clin. Path.*, 1961, **14** (2), 202–204.—Blood (3 ml) and 1·25% $ZnSO_4$ soln. in 0·03125N-H_2SO_4 (24 ml) are mixed and shaken to obtain complete haemolysis, and 0·75N-NaOH (3 ml) is then added. The mixture is shaken again and filtered (S. & S. No. 5893, Blauband, paper), 10 ml of the filtrate, followed by 2% *p*-dimethylaminobenzaldehyde soln. in 96% ethanol (10 ml), is transferred to a 25-ml flask, and the volume is made up with water. The extinction is read any time after 10 min. at 420 or 435 mµ. The procedure for urine is the same, but the specimen should be diluted if the urea concn. is >1000 mg per 100 ml. R. A. BRENAN

3867. **Chromatographic separation and purification of folic acid analogues.** V. T. Oliverio (Nat. Cancer Inst., Nat. Inst. Health, Bethesda, Md., U.S.A.). *Anal. Chem.*, 1961, **33** (2), 263–265.—Folic acid analogues are separated on diethylaminoethylcellulose anion-exchange columns by linear gradient elution with phosphate buffer at pH 8. The fractions are monitored with 254-mµ light and those giving peak transmittance are pooled and the absorption spectrum from 230 to 400 mµ is determined. The purity of a single compound is determined from the extinction at a given wavelength. G. P. COOK

3868. **Determination of δ-aminolaevulic acid according to Shuster.** T. Malinowska Dept. of Health Protection, Inst. of Nucl. Res., Warsaw, Poland). *Chem. Anal., Warsaw*, 1960, **5** (6), 1049–1054.—Shuster's picrate method (*Anal. Abstr.*, 1957, **4**, 219) is modified. *Procedure*—Trichloroacetic acid is added to a 0·5% homogenate of

liver (2 ml) protein is filtered off, and 0·02M-picric acid (0·3 ml) and 2·5N-NaOH (0·5 ml) are added to the filtrate. The mixture is heated in a water bath at 20° for 7 min., and 8N-HCl (1 ml) is added. After 10 min. the excess of picric acid is removed by shaking with ethyl ether (2 × 10 ml), for 2 min. and light petroleum (10 ml) for 1 min., and the extinction is measured at 420 mμ against a blank; 0·01 μmole of δ-aminolaevulic acid can be determined in 4 ml of sample. B. K.

3869. **Continuous polarographic determination of α-amino-acids.** W. J. Blaedel and J. W. Todd (Chem. Dept., Univ. Wisconsin, Madison, U.S.A.). *Anal. Chem.*, 1961, **33** (2), 205–207.—The method is based on the reaction of α-amino-acids with copper phosphate to produce an equivalent amount of Cu^{2+}, which are determined polarographically as the EDTA complex. Concn. of up to 6mM can be determined with a coeff. of 3% or variation greater for small amounts. The method was applied to the continuous measurement of ion-exchange column percolates. G. P. Cook

3870. **Quantitative chromatographic methods. VI. Improved procedure for determination of amino-compounds on paper chromatograms.** E. Tigane, E. H. M. Wade, J. T. Wong and C. S. Hanes (Dept. of Biochem., Univ. Toronto, Ontario, Canada). *Canad. J. Biochem. Physiol.*, 1961, **39** (2), 427–437.—For the detection and localisation of amino-acid spots on chromatograms, a fresh dip-reagent consisting of ninhydrin (125 mg), glacial acetic acid (25 ml), collidine (20 ml) and ethyl acetate (955 ml) is used. For quant. determination the spots are cut from the dried paper, wetted with methanolic borate buffer soln. [boric acid (18 g), 6N-aq. KOH (65 ml) and methanol (935 ml)] and dried in air at 40° to eliminate NH_3. The dried portions of paper are then treated, in an atmosphere of N, with the reagent previously described (Matheson *et al.*, *Anal. Abstr.*, 1961, **8**, 3990), to which one-tenth of its vol. of water is added, and the colour is developed by heating at 100° for 20 min. The soln. is then suitably diluted with 50% aq. ethanol and the extinction is measured at 570 mμ (440 mμ for proline and hydroxyproline). The yields of Ruhemann's purple from the paper spots of most amino-acids were found to be close to the stoicheiometric values.

VII. Isolation of amino-acids from serum and other fluids. C. K. Harris, E. Tigane and C. S. Hanes. *Ibid.*, 1961, **39** (2), 439–451.—A small-scale method, based on the use of miniature ion-exchange columns, is described. The resin used is Dowex 50 (H^+ form); about 350 mg of moist resin is suitable for treating 5 ml of serum or plasma, which is diluted 1:1 with water and adjusted to pH 2·0 to 2·5 with 8N-acetic acid. Elution is with 2N-triethylamine in 20% aq. acetone. The eluate is tested with bromocresol green, a change from yellow to yellow-green indicating the appearance of the amino-acid fractions, which may be quant. recovered in fractions of 1 to 2 ml. After evaporation to dryness over conc. H_2SO_4 *in vacuo*, the residue is dissolved in 100 μl of water and chromatographed on paper. Strongly acid compounds (*e.g.*, cysteic acid and taurine) are not recovered with the amino-acids by this procedure. With urine and some other biological fluids, ninhydrin-reacting compounds other than amino-acids may also be isolated, and may require special separation procedures. D. G. Moss

3871. **Gas chromatography of silylated amino-acids.** K. Rühlmann and W. Giesecke (Inst. f. Verfahrenstech. d. org. Chem., Leipzig). *Angew. Chem.*, 1961, **73** (3), 113.—The amino-acid salts are treated with trimethylchlorosilane, or the free amino-acids with *NN*-dialkyl-*N*-trimethylsilylamine, to yield the trimethylsilyl esters of the *N*-trimethylsilyl amino-acids, which can be separated by gas chromatography. N. E.

3872. **Ninhydrin assay in the presence of thiol [mercapto] compounds.** J. R. Whitaker (Dept. of Food Sci. and Technol., Univ. of Calif., Davis, U.S.A.). *Nature*, 1961, **189**, 662–663.—Mercapto-compounds such as cysteine, mercaptoethanol and 2,3-dimercaptopropan-1-ol interfere with the colorimetric determination of amino-acids with the ninhydrin reagent of Moore and Stein (*Anal. Abstr.*, 1955, **2**, 986). Leucine (≃ 0·2 μmole) and other amino-acids can be quant. determined if *N*-ethylmaleimide (4 μmoles) is added and if the amount of hydrindantin in the reagent is doubled. A. R. Rogers

3873. **Use of paper electrophoresis for the characterisation and determination of glycine. Applications.** J. Saint-Blancard and J. Storck (Centre de Transfusion-Réanimation de l'Armée, Clamart, Seine, France). *Ann. Pharm. Franç.*, 1960, **18** (10), 711–714.—A rapid method for separation and determination of glycine in protein hydrolysates, or in materials in which it is used for the stabilisation of γ-globulin, is described. *Procedure*—A sample containing up to 12 μg of glycine is spotted on to a sheet of Arches-302 paper (395 mm × 275 mm) together with 5 spots of standard soln. of glycine. Electrophoresis is carried out in a soln. made by making up 58 ml of glacial acetic acid and 26 ml of 25% formic acid to 2 litres with water. A voltage of 240 V is applied and the glycine migrates to the cathode. For qual. detection, the dried paper is dipped in 5% ethanolic ninhydrin made alkaline with 0·5 ml of N-aq. KOH and heated at 80° for 20 min. A table is given of the relative movement of other amino-acids. Unchanged proteins remain on the starting line. For quant. determination, the violet ninhydrin spot is extracted with 0·1% aq. $CdCl_2$ in 40% aq. methanol, and the extinction of the resulting pink soln. is measured at 505 mμ, against the slightly yellowish extract of the paper alone as blank. E. J. H. Birch

3874. **Quantitative determination of haemoglobin A_2 using paper electrophoresis.** R. N. Ibbotson and B. A. Crompton (Div. Clin. Path., Inst. Med. and Vet. Sci., Adelaide, S. Australia). *J. Clin. Path.*, 1961, **14** (2), 164–166.—The blood samples are collected, with EDTA (dipotassium salt) as anti-coagulant, haemolysed with water and toluene, and converted into carboxyhaemoglobin. Electrophoresis is carried out in vertical tanks with strips (25·5 cm × 4·0 cm) of Whatman No. 3 MM paper and tri(hydroxymethyl)methylamine buffer adjusted to pH 8·6 with boric acid. The treated samples (20 μl) are applied to the strips, which are then moistened with buffer on both sides to within 0·25 in. of the point of application. After passing a current of 225 V and 2 mA per strip for 16 hr., the strips are dried at 90° to 100°, fixed for 10 min. in fresh 10% $HgCl_2$ soln. and 10% glacial acetic acid in ethanol, re-dried, washed twice in water for 10 min. and then dried again. They are then stained for 10 min. in 1% bromophenol and 1% acetic acid in ethanol, washed several times in

0·5% acetic acid in 25% ethanol, and dried. The stained bands are cut out, and eluted with 1·5% Na_2CO_3 soln. in 50% methanol, and the extinctions of the eluates are read at 595 mμ in a spectrophotometer. R. A. BRENAN

3875. **Tris buffer for differentiation between haemoglobins C and E and separation of haemoglobins S from F and 'lepore' from A.** H. Lehmann and A. Sharih (Dept. of Path., St. Bartholomew's Hosp., London). *J. Clin. Path.*, 1961, **14** (2), 200–201.—The use of tri(hydroxymethyl)methylamine buffer in addition to the more usual barbiturate buffer in the investigation of haemoglobins is advocated. R. A. BRENAN

3876. **Rapid method for the estimation of serum haptoglobin.** D. S. Rowe (Dept. of Exp. Path., Univ. of Birmingham, England). *J. Clin. Path.*, 1961, **14** (2), 205–206.—The serum mixed with varied amounts of carboxyhaemoglobin (ranging from 0·2 to 1·6 mg per ml of serum) is placed in a series of holes in agar gel on a glass plate and subjected to electrophoresis at 240 V and 12 mA for 45 min. The plate is then placed in benzidine stain [0·2% of benzidine in 0·5% acetic acid; immediately before use, 0·2 ml of 30% (w/v) H_2O_2 soln. is added to each 100 ml]. Haptoglobin-bound haemoglobin moves slightly towards the anode and free haemoglobin towards the cathode. R. A. BRENAN

3877. **Staining lipoproteins before their separation by paper electrophoresis.** V. F. Bogoyavlenskiĭ and D. N. Rozenshtein. *Vracheb. Delo*, 1960, (8), 125–126; *Ref. Zhur., Khim., Biol. Khim.*, 1960, (6), Abstr. No. 6S84.—*Procedure*—Add Sudan I (C.I. Solvent Yellow 14) or Sudan black (C.I. Solvent Black 3) soln. (0·25 g in 100 ml of ethanol) (0·1 ml) to fresh blood serum (0·5 ml) and set it aside for 30 min. Subject the coloured serum (0·05 to 0·1 ml) to electrophoresis, and analyse the electropherogram by the usual methods. K. R. COOK

3878. **Spectrophotometric determination of nucleic acids in higher plants.** S. V. Netupskaya, Yu. V. Peruanskiĭ and V. G. Konarev. *Byull. Nuklein. Obmena u Rasteniĭ*, 1959, 148–153; *Ref. Zhur., Khim., Biol. Khim.*, 1961, (3), Abstr. No. 3S27.—Grind leaves (1 to 2 g), seeds, or starch grains as finely as possible in a soln. (5 ml) made 0·001N with respect to H_2SO_4 in 80% ethanol, dilute to 20 ml with the same soln., filter, and wash the residue with 80% ethanol, acetone, and ethanol - ether (1 : 1) to remove chlorides, free purines, pigments and most of the lipid content. Add N-H_2SO_4 (20 ml) to the residue and hydrolyse it in a boiling-water bath for 1 hr. to obtain the purines from the nucleic acids. Add 0·5N-$AgNO_3$ (1 ml) to the hydrolysate (10 ml), place the mixture in a refrigerator for 1 hr., then centrifuge, wash the residue with 0·01N-H_2SO_4 satd. with Ag_2SO_4 and dissolve it in N-HCl (1 ml). Set the soln. aside for 1 hr., centrifuge, and measure the supernatant liquid photometrically for its purine content. Maximum reproducibility is attained with a purine concn. of 4 to 12 μg per ml. K. R. COOK

3879. **Detection of ribonucleic acid with a methyl green - pyronine mixture.** R. A. Simakova. *Arkh. Patol.*, 1960, **22** (6), 81–82; *Ref. Zhur., Khim., Biol. Khim.*, 1961, (1), Abstr. No. 1S34.—The reagent normally used for the detection of ribonuclease is modified as follows—0·5% methyl green soln. (4 ml) which has been purified by extraction with $CHCl_3$ is mixed with 1% pyronine G soln. (9 ml) The soln. is diluted to 25 ml with H_2O, and acetate. buffer (pH 4·8) (25 ml) is added. The reagent is stable for a week if stored in a refrigerator. K. R. COOK

3880. **Quantitative micro-determination of cholesterol using tomatine as precipitating agent.** J. J. Kabara, J. T. McLaughlin and C. A. Riegel (Dept. of Chem., Univ. Detroit, Mich., U.S.A.). *Anal. Chem.*, 1961, **33** (2), 305–307.—Radioactive and non-radioactive cholesterol in blood and tissue samples are determined with good specificity with tomatine as the precipitating agent. Radioactive cholesterol is measured by liquid scintillation counting and the non-active material by a colorimetric method with the Liebermann - Burchard reagent. (*Cf.* Kabara, *Anal. Abstr.*, 1958, **5**, 669.) G. P. COOK

3881. **Determination of cholesterol and squalene by gas chromatography.** H. J. O'Neill and L. L. Gershbein (Armour Res. Found. of Illinois Inst. of Technol., Chicago, U.S.A.). *Anal. Chem.*, 1961, **33** (2), 182–185.—A high-temperature technique is described for determining cholesterol and squalene in scalp sebum, ovarian dermoid cysts, placental lipids, basking-shark oil, tall oil and synthetic mixtures containing squalane. The analysis is carried out at 332° on a 2-ft. column of 30% Apiezon-L grease on 30 to 60-mesh support, with a platinum-filament katharometer detector. Helium at 50 ml per min. is the carrier gas and the analysis, made on the unsaponified fraction of the sample, is complete within 10 min. Results for cholesterol on various samples containing from 2 to 24% of cholesterol show excellent agreement with results obtained by the Liebermann - Burchard colorimetric procedure, having an over-all deviation of ±0·7%. No evidence of thermal degradation is observed among any of the samples or components analysed. C. B. BAINES

3882. **An evaluation of the use of digitonin for the analysis of faecal sterols.** W. W. Wells and P. A. Mores (Biochem. Dept., School of Med., Univ. of Pittsburgh, Pa., U.S.A.). *Nature*, 1961, **189**, 483–484.—Incompleteness of pptn. of coprostanol (5β-cholestanol) digitonide in the solvents used in the procedure of Sperry and Webb (*J. Biol. Chem.*, 1950, **187**, 97) may account for some of the quantities reported as "non-3β-hydroxyl faecal sterols." The rejected washings in the Sperry and Webb procedure may contain up to 40% of the original 5β-cholestanol. Chromatographic methods of analysis are preferred (*cf.* Coleman *et al.*, *Anal. Abstr.*, 1956, **3**, 3431). A. R. ROGERS

3883. **Simplified quantitative analysis by countercurrent distribution. I. Analysis of one and of two stages.** G. Pancrazio and P. Del Grande; **II. Apparatus with lower mobile phase: analysis of binary mixtures of oestrogens.** M. Vitali, G. Sbarigia and G. Pancrazio; **III. Apparatus with two mobile phases: analysis of mixtures of corticosteroids.** G. Pancrazio and P. Del Grande (Ist. Terapeutico Romano, Rome). *Ann. Chim., Roma*, 1960, **50** (12), 1730–1752; 1753–1759; 1760–1768.—Two simplified procedures for countercurrent distribution analysis are proposed and sources of error in the determination are considered. Apparatus with a lower mobile phase or two mobile phases is described, and applications

to the analysis of binary mixtures of oestradiol and its derivatives, and of binary and ternary mixtures of corticosteroids, are shown. L. A. O'NEILL

3884. **Diagnostic preparation for the determination of serum alkaline phosphatase.** Warner-Lambert Pharmaceutical Co. Brit. Pat. 863,739; date appl. 10.7.58. U.S.A., date appl. 11.7.57.—A preparation in powder or tablet form for the determination of serum alkaline phosphatase comprises an alkali-metal or alkaline-earth-metal salt of phenolphthalein phosphate (1·5%), a magnesium salt, *e.g.*, $MgSO_4$ (0·1%), and a buffer to maintain the pH of the serum at 9 to 11, *e.g.*, tri(hydroxymethyl)methylamine (98·4%). J. M. JACOBS

3885. **Methods for the determination of some transaminase activities in biological fluids.** F. Salvatore, V. Bocchini and F. Cimino (Biochem. Dept., Univ. Naples, Italy). *Enzymologia*, 1961, **22** (6), 357–363.—A method is described for the determination of the transaminase activity of materials such as blood and cerebrospinal, ascitic, pleural and synovial fluids. Aliquots of amino-acid soln. (0·5 ml of 0·2M-L-aspartic acid or L-alanine) and 0·2 ml of 0·1M-α-oxoglutaric acid are placed in centrifuge tubes and made up to 2 ml with phosphate buffer (pH 7·4). At 37° an aliquot of the sample is added and the temp. is maintained for 10 min.; the reaction is then stopped by the addition of 50% trichloroacetic soln. (0·2 ml). With aspartic acid, 0·2 ml of fresh aniline - 80% citric acid soln. (1:1) is added to decarboxylate the oxalacetic acid formed; 1 ml of 2,4-dinitrophenylhydrazine soln. (0·1% in 2·5N-HCl) is then added and allowed to react for 5 min. at 37°. The colour is extracted with xylene (2 ml), an aliquot (1 ml) is mixed with 25% ethanolic KOH soln. (6 ml) and the extinction is measured at 490 mμ. Alanine - oxoglutaric and aspartic - oxoglutaric transaminase activities can be determined directly in blood plasma or serum, but other fluids need preliminary concentration by freeze-drying. Typical values for samples from diseased subjects are given and the technique is suggested as an aid to diagnosis. J. R. HUDSON

3886. **Assay of human plasminogen with casein as substrate.** M. Derechin (Lister Inst., Chelsea Bridge Rd., London, England). *Biochem. J.*, 1961, **78** (2), 443–448.—A triphasic graph is obtained when the proteolysis of casein by plasmin is followed by measurement of the increase in material which is sol. in $HClO_4$ and has an absorption max. at 276 mμ. Only the second part of the graph is linear. Unreliable results are obtained in the assays of plasminogen prep. based on single samples taken after a definite time of proteolysis, because of the influence of the lag period of the reaction before the linear portion of the graph is reached. The length of this lag period increases with increase in the concn. of the substrate or with decrease in enzyme concn. The slope of the linear part of the graph is proportional to enzyme activity and is practically independent of substrate concn. over a 10-fold range. A standardised procedure is described in which the proteolysis is carried out at 40° and pH 7·6. This gives reliable results when these are calculated from the slope of the linear part of the reaction graph. J. N. ASHLEY

See also Abstracts—**3561**: *Section Vb.* Products of alkali treatment of keratin. **3584**, Simultaneous estimation of nuclides. **3771**, **3772**, Titration of mercapto-groups. **3779**, Gas-chromatographic analysis of sugar mixtures. **3803**, Determination of carcinogenic hydrocarbons. **3896**, Triterpenoids and saponins in plants. **3897**, Determination of corticosteroids. **3903**, Continuous measurement of dissolved O in fermentation media. **3911**, *N*-Phthaloylglutamimide in blood. **3922**, Glycogen in oysters. **3954**, Ascorbic and dehydroascorbic acids in plants. **3959**, Amino-acids in natural water. **3978**, Automatic analysis of body fluids.

Pharmaceutical analysis

3887. **Use of anhydrous propionic acid as solvent for titration of some alkaloids.** S. Przyszlakowski (Dept. of Inorg. Chem., Med. Acad., Lublin, Poland). *Acta Polon. Pharm.*, 1960, **17** (5), 395–398.—Brucine, codeine, diamorphine, narceine, narcotine, quinine and veratrine were determined by means of potentiometric titration with $HClO_4$ in anhyd. solvents. Of the two solvents used, anhyd. acetic acid and anhyd. propionic acid, the latter was the more satisfactory, especially for the titration of weak bases with 0·01N-$HClO_4$. B. K.

3888. **The use of paper chromatography for checking methods for the determination of morphine in opium. I.** J. Büchi and R. Huber (Pharm. Inst., Eidg. Tech. Hochsch., Zürich). *Pharm. Acta Helv.*, 1961, **36** (1–2–3), 119–130 (in German).—The method of the Ph. Helv. V for the extraction of morphine from opium and some modifications have been critically examined by paper-chromatographic techniques. A. R. ROGERS

3889. **Application of gas chromatography to the determination of cocaine, arecoline and pethidine.** C. Stainier and E. Gloesener (Lab. d'Analyse des Medicaments, Univ. Liége, Belgium). *Farmaco, Ed. Prat.*, 1960, **15** (12), 721–731 (in French).—Arecoline and cocaine are methyl esters and pethidine is an ethyl ester. The application of gas chromatography to the determination of these compounds depends on the measurement of the volatile methanol and ethanol resulting from hydrolysis. Dissolve arecoline hydrobromide (50 mg) in 94% ethanol containing 3·5% KOH (1 ml) and add a known amount of benzene (5 to 10%) as an internal standard. Hydrolyse the mixture in a 10-ml stoppered flask for 1 hr. on a boiling-water bath. After cooling, take 0·02 ml for chromatography, with Carbowax 1500 and triethanolamine as stationary phase, and H as mobile phase at 70°; detection is by thermal conductivity. For cocaine, 60 to 70 mg of the hydrochloride is hydrolysed with 5% ethanolic KOH, and for pethidine, propanol is used instead of ethanol in the hydrolysis. J. I. M. JONES

3890. **Quantitative paper-chromatographic determination of alkaloids from the thorn apple (*Datura stramonium*).** N. Mešiček (Inst. Org. Chem., Univ., Ljubljana, Yugoslavia). *Mikrochim. Acta*, 1961, (2), 283–288 (in German).—Hyoscyamine and atropine can be separated from hyoscine, but not from one another, by ascending chromatography on buffered paper (pH 7·0 to 7·6) with water-saturated butanol or amyl alcohol as mobile phase. The separated alkaloids are detected by spraying the paper with Dragendorff reagent, and determined colorimetrically by extracting the excised areas from the chromatogram with acetic anhydride and

measuring the extinction at 485 mμ. The results obtained on extracts of stramonium are 40% lower than titrimetric values owing to the presence of basic substances other than alkaloids which interfere in the titration. W. T. CARTER

3891. **Determination of *N*-*p*-phenylbenzylatropinium bromide (Gastripon) and its administration forms.** Z. Jung and H. Petříková (State Inst. for Control of Drugs, Prague). *Českosl. Farm.*, 1961, **10** (2), 72–75.—The characteristic absorption of *N*-*p*-phenylbenzylatropinium bromide (**I**) (the active ingredient of Gastripon) with a max. at 257 mμ was used for the determinations in methanol (70%), in a mixture of methanol and aq. NH_3 (25%) (7:3) and in a soln. of N-HCl in methanol (70%). For the determination of **I** in tablets or injections, a preliminary separation is carried out on Dowex 50-X2. *Procedure for tablets*—Heat the powdered tablets (≃5 mg of **I**) with methanol (70%) (30 ml) in a 50-ml flask for 3 min. on a water bath with occasional shaking, cool, dilute with methanol (70%) to vol., mix, centrifuge and pass 12 ml through a column of Dowex 50-X2 (1 ml per min.); wash the column with methanol (70%) (25 ml), then heat it to 50° and elute **I** with 100 ml of N-HCl in methanol (70%) (1 ml per min.). Measure the extinction at 257 mμ and compare with a blank. The same procedure can be used for Gastripon injections containing **I** and urethane. J. ZÝKA

3892. **Use of Reinecke's salt for the assay of ipecacuanha root.** B. Kamiński and J. Wierzbowicz (Drug Res. Inst., Warsaw). *Acta Polon. Pharm.*, 1960, **17** (5), 387–393.—A method based on the separate pptn. of phenolic and non-phenolic alkaloids, and proposed for the next edition of Pharm. Polon. (*cf.* Borkowski and Frenclowa, *Ibid.*, 1956, **13**, 161, 169) was investigated. It was found that emetine reineckate is partly sol. in H_2O and emetine is partly soln. in $Ba(OH)_2$ soln., used for the separation of phenolic alkaloids. This accounts for the low accuracy of the proposed method and the non-repeatable results. B. K.

3893. **Determination of alkaloids in *Ephedra equisetina*.** R. A. Vidozminena. *Farm. Zhur.*, 1960, (3), 43–45; *Ref. Zhur., Khim., Biol. Khim.*, 1961, (6), Abstr. No. 6S94.—*Procedure*—Add 1% H_2SO_4 (100 ml) to ground *Ephedra equisetina* (10 g) and agitate the mixture for 1 hr. Filter, neutralise the filtrate to litmus with 30% NaOH soln. and extract the alkaloids with ether (30 ml, 3 × 25 ml). Combine the extracts and dry them with anhyd. Na_2SO_4, filter, and evaporate the filtrate to 3 to 5 ml; add 0·1N-HCl (20 ml) and distil off the residual ether. Titrate the uncombined HCl with 0·1N-NaOH to methyl red and calculate the alkaloid content; 1 ml of 0·1N-HCl ≡ 0·0165 g of total alkaloids. K. R. COOK

3894. **Analysis of ergot alkaloids. III. Quantitative determination of alkaloids in Secale concentratum (Stada).** M. Klavehn, H. Rochelmeyer and J. Seyfried (Pharm. Inst. der Johannes-Gutenberg-Univ., Mainz). *Dtsch. ApothZtg*, 1961, **101** (4), 75–78.—The sample, containing 0·2 to 1 mg of total alkaloid and dissolved in dichloromethane - methanol (10:1), is applied along a line 7 cm long on paper impregnated with formamide - ethanol (2:3), and chromatographed with benzene saturated with formamide or $CHCl_3$ - ethanol (19:1) for water-insol. or water-sol. alkaloids, respectively. Zones are detected by irradiation with u.v. light, then cut out and individually eluted with ethyl acetate - dimethylformamide (20:1). The ethyl acetate is evaporated, the residue is dissolved in acetic acid, and diluted with water, and the alkaloid is determined spectrophotometrically. Separation on thin films of silica gel with $CHCl_3$ - ethanol (10:1) as solvent is also described. As little as 0·1 μg of alkaloid may be detected by spraying the chromatogram with *p*-dimethylaminobenzaldehyde in HCl and drying at 105°. A. G. COOPER

3895. **Determination of reserpine. II. The nitrite method.** O. Weis-Fogh (Danmarks Apotekerforening, Copenhagen, Denmark). *Arch. Pharm. Chemi*, 1960, **67** (9), 425–443.—The method of Szalkowski and Mader (*Anal. Abstr.*, 1957, **4**, 654) and the modifications of Banes *et al.* (*Anal. Abstr.*, 1957, **4**, 1324) are critically examined, together with the influence of four antioxidants. The accuracy is somewhat less in the presence of antioxidants, but the results are reproducible to within ±2%. P. PEDERSEN

3896. **Triterpenoid compounds in plant materials. III. Paper chromatography of triterpene alcohols.** B. Pasich (Dept. of Pharmacog., Med. Acad., Poznań, Poland). *Dissert. Pharm., Krakow*, 1960, **12** (3), 201–210 (in English).—A mixture of 6 triterpenoids (aescigenin, primulagenin A, betulin, lupeol, arnidenediol and α-lactucerol) is separated by means of paper chromatography. The R_F values of the components on Whatman No. 1 paper, impregnated with aluminium hydroxide, in such solvents as benzene, cyclohexane, toluene and xylene, are given, and colour reactions with 8 reagents are tabulated. Triterpenoid compounds are detectable on chromatograms in amounts of 5 to 10 μg per sq. cm, and identification is possible, by comparison with standards, of 25 to 50 μg per sq. cm.

IV. Chromatographic characterisation of the more important saponins in medicinal plants. B. Pasich. *Ibid.*, 1961, **13** (1), 1–10 (in English).—Saponins isolated from the seeds of *Aesculus hippocastanum* L. (**I**), the roots and rhizomes of *Saponaria officinalis* L. (**II**), the roots of *Gypsophila paniculata* Fisch. (**III**), the roots and rhizomes of *Primula officinalis* L. (**IV**), the flowers of *Calendula officinalis* L. (**V**), the bark of *Quillaia saponaria* Molina (**VI**), the roots and rhizomes of *Polygala senga* L. (**VII**), and *Herniaria glabra* L. herb (**VIII**) were investigated chromatographically. Three solvent systems were used, the best results being given with n-butanol - acetic acid - H_2O (6:1:3), with the ascending technique, for 15 hr. The saponin spots were revealed with 5 colour reactions and 2 haemolytic tests. The reaction with alcoholic tungstophosphoric acid soln. was the most valuable for the identification. The limit of detection is from 5 to 40 μg. R_F values and colours of the spots in daylight and u.v. with the various reagents are tabulated. It was found that the saponin of **V** contains three triterpenoid glycosides, and the saponins of **II**, **III**, **VI**, **VII** and **VIII** each contain two components. Aescinol (obtained from **I**) and primulic acid (from **IV**) each contains only one triterpenoid component. B. K.

3897. **Determination of corticosteroids in their pharmaceutical forms by means of *p*-nitrosodimethylaniline.** J. Verdier (Centre de Rech., Roussel-Uclaf, Paris, France). *Ann. Pharm. Franç.*, 1960, **18** (11), 795–799.—The speed of

reaction of a number of corticosteroids with *p*-nitrosodimethylaniline is determined with a view to the application of the Pesez reaction (*cf.* Pesez and Robin, *Ibid.*, 1959, **17**, 624). *Procedure*—With the more rapidly reacting compounds, add to 1 ml of the ethanolic soln. of the steroid (obtained by procedures which are outlined) 0·5 ml of 0·1% ethanolic *p*-nitrosodimethylaniline and then, after 5 min. at 0°, 0·5 ml of 0·1N-NaOH. After setting the mixture aside for 1 to 6 hr. (a table of times for various compounds is given) in the absence of light, at 0°, add 2 ml of borate buffer (pH 9·8), 5 ml of 0·1% ethanolic phenol and 0·5 ml of fresh aq. $K_3Fe(CN)_6$, and after 10 min. at 20° ± 2° measure the extinction at 650 mμ. With the less rapidly reacting steroids (hemisuccinic, cyclohexanecarboxylic or *m*-sulphobenzoic esters), add to 1 ml of the steroid soln. 1 ml of the *p*-nitrosodimethylaniline soln. and, after 5 min. at room temp. (25°), 1 ml of 0·1N-NaOH. After 1 to 2 hr. at room temp., shaded from the light, complete the determination as described above. E. J. H. BIRCH

3898. **Simplifications of the colorimetric hydroxylamine method for penicillin determination in fermentation media and finished salts.** L. Carta-de Angeli, M. T. Ventura and F. Dentice di Accadia (Ist. Sup. San., Centro Int. di Chimica Microbiol., Roma, Italy). *R.C. Ist. Sup. Sanit.*, 1960, **23** (10–11), 915–923.—Penicillin is determined by reaction with a neutralised ethanolic soln. of hydroxyammonium chloride and a 20% soln. of $(NH_4)_2SO_4.Fe_2(SO_4)_3$. The procedure is applicable to an aq. or ethanolic soln. of salts or to the n-butanol extract from fermentation media, previously adjusted to pH 2. A blank is not necessary except with highly coloured extracts, when a dulpicate extract, inactivated by boiling for 5 min. after acidification to pH 2, is satisfactory. The method is reproducible to within ± 2%, and is recommended for routine analyses.

E. C. APLING

3899. **Determination of tetracycline and chlortetracycline when present together.** E. N. Druzhinina. *Antibiotiki*, 1961, **6** (2), 167–172.—The cup-plate method is proposed for the determination of tetracycline (**I**) and chlortetracycline (**II**) in medicinal preparations and in *Actinomyces aureofaciens* culture fluids. The principle of the method is to determine the total activity (expressed in units of **I**) and to destroy **II** so that **I** can be determined alone; **II**, calculated by difference, is expressed in units of **I**. To determine **I**, use a medium (pH 8 to 8·2) consisting of 1 to 1·5% agar containing 135 mg of amino-N per 100 ml and 1% of glucose. Add the test culture of a spore-forming bacillus (*e.g. Bacillus subtilis*) (30 to 40 million organisms per ml of medium) to the medium at 65° to 70° and add 10 ml of the seeded medium to each cup. Dissolve dry test samples in 0·01N-HCl to obtain a concn. of 1 mg per ml. Dilute culture fluids and test soln. in NaOH - citrate buffer (pH 7·8 to 8) to ≃2 units of **I** per ml. Prepare standard soln. of 2 units of **I** per ml in the same buffer. To determine the total activity of **I** plus **II** in comparison with standard **I** soln. dilute all test and standard soln. in an HCl - citrate buffer (pH 3 to 3·2); use the same agar medium as before but at neutral pH. Tabulated results for culture fluids and dry samples by the spectrophotometric method are in good agreement with the results obtained by this method; it is possible to control fermentation and the various stages of purification with the same precision as with the spectrophotometric method.

K. R. COOK

3900. **Simplified spectrophotometric assay of griseofulvin in fermentation samples.** C. Daly (Glaxo Lab. Ltd., Ulverston, Lancs., England). *Analyst*, 1961, **86**, 129–131.—At 7 equally spaced wavelengths (288, 290 . . . 300 mμ) the extinctions of a standard soln. of griseofulvin in butyl acetate and of the sample in the same solvent are measured for all but the middle wavelength. Hence by a simple equation the proportion of griseofulvin in the sample is calculated. The method is similar in principle to that of Ashton *et al.* (*Ibid.*, 1956, **81**, 220, 225), but avoids complex calculations and has the advantage that the standards may be set up at the same time as the sample. A. O. JONES

3901. **Differential assay for mitomycin A and C.** A. Gourevitch, V. Z. Rossomano and J. Lein (Bristol Lab., Syracuse, N.Y., U.S.A.). *Antibiot. & Chemother.*, 1961, **11** (1), 48–51.—The method is based on the observation that mitomycin A has 20 times the activity of mitomycin C against *Bacillus subtilis* ATCC 6633, whereas the two antibiotics have identical activities against *Klebsiella pneumoniae* FDA 602. In the agar-diffusion assays described, dose - response curves with *B. subtilis* are linear and parallel with 0·4 to 10 and 0·001 to 0·02 μg per ml, respectively. With *K. pneumoniae*, the linear range for each antibiotic is 0·5 to 60 μg per ml. Results are read off from a nomogram.

W. H. C. SHAW

3902. **Adaptation of the Quebec colony-counter for antibiotic zone reading.** N. Grecz (Chicago Univ., Ill., U.S.A.). *Antibiot. & Chemother.*, 1961, **11** (1), 46–47.—A description is given of the preparation and use of a simple inexpensive transparent measuring scale made from commercial (U.S.) cross-hatched acetate sheet.

W. H. C. SHAW

3903. **Continuous measurement of dissolved oxygen in fermentation media in the presence of micro-organisms.** G. Gualandi, G. Morisi, G. Ugolini and E. B. Chain (Ist. Sup. San., Centro Int. di Chim. Microbiol., Roma, Italy). *R.C. Ist. Sup. Sanit.*, 1960, **23** (10–11), 822–868.—The construction and use of two specially designed amalgamated silver electrode systems is described, and detailed constructional diagrams are given. The first system, suitable for semi-continuous measurements in shake-flasks or in fermentation vessels, consists of a disc anode (20 mm × 1·5 mm) and a silver-wire cathode, set into a cylinder of epoxide resin (Araldite D), covered with a film of collodion (≃0·3 μ), and sterilised by immersion in 15% formaldehyde soln. for 30 min. Equilibration of the electrodes with the soln. takes several minutes, but the sensitivity remains constant if current is passed for ⩾ 60 sec. at intervals of ⩽ 20 min. In the second system, designed for continuous measurements in large fermenting vessels, a wire microcathode, the surface of which is continuously cleansed by means of a velvet-covered rotating disc, is used. The electrode system forms a compact unit which will withstand sterilisation by steam at 125° for 60 min. The two systems give comparable results when used to measure dissolved oxygen during the course of a variety of fermentations under turbulent conditions. E. C. APLING

nitropropane and nitrobutane. *Section VI*, Gas chromatography of higher alcohols and paraffins. Paper chromatography of di- and tri-hydric phenols. Starch hydrolysis. Poly(alkyl methacrylates). Fatty acids in lubricating grease and soap. *Section VIIa*, Spectrophotometry of pinacyanol and pinakryptol green. **3569**, Purification of dimethylformamide. **3572**, Analysis of gas mixtures. **3640**, C in org. compounds. **3656**, Analysis of Pb tannate. **3882**, Paper chromatography of sugar phosphates. **3930–3933**, Dyes for use in foods. **3956**, Chlorinated aliphatic hydrocarbons in air. **3985**, Apparatus for Kjeldahl method. **3989**, Chromatographic reagents for nitrogenated compounds and carbohydrates. **3994**, Gas chromatography of polyphenyls. **3998**, Flame ionisation chromatography of hydrocarbon mixtures. **4023**, Titration of acids and bases with metal - metal oxide electrodes.

4.—BIOCHEMISTRY

INCLUDING DRUGS, FOOD, SANITATION, AGRICULTURE

Biological fluids, animal and vegetable tissues

3847. **Simple method of estimating the tritium content of biological samples.** G. G. Steel (Phys. Dept., Inst. of Cancer Res., Belmont, Surrey, England). *Int. J. Appl. Radiation and Isotopes*, 1960, **9** (1–4), 94–99.—The sample, mixed with CuO, is heated in a tube that also contains a layer of heated CuO through which the H_2O produced is passed; a layer of a mixture of glucose and CuO is heated after the combustion of the sample and the H_2O produced assists the transfer of the tritiated H_2O to the other end of the tube, which is kept at −65°. The tritiated H_2O is then added, with ethanol, to the liquid scintillator and the activity is measured with a counter having an efficiency of 10% and a background of 10 counts per sec.; a standard addition of ^3H is then made and the activity is recorded again. The recovery of ^3H is >95%. The time required for a determination is 30 min. G. J. HUNTER

3848. **Rapid assay procedures for tritium-labelled water in body fluids.** B. E. Vaughan and E. A. Boling (U.S. Naval Radiological Defense Lab., San Francisco, Calif., U.S.A.). *J. Lab. Clin. Med.*, 1961, **57** (1), 159–164.—In the first method described, the sample (0·5 to 2 ml) is vacuum-sublimed in a special small glass flask to eliminate errors due to light-quenching substances in the sample. The melted sublimate is then diluted with a scintillation liquid for counting. When a larger sample is available, or sublimation is impracticable, an alternative method requiring internal standardisation with tritiated water may be employed; this gives slightly less accurate results and necessitates a separate water determination on the sample. The application of the methods for determining total body water, and the results obtained, are discussed.
W. H. C. SHAW

3849. **Determination of fall-out caesium-137 in animal and plant tissues.** C. Blincoe (Dept. Agric. Chem., Univ. Nevada, Reno, U.S.A.). *J. Agric. Food Chem.*, 1961, **9** (2), 127–129.—The residue obtained from the sample by dry-ashing at 550° and several subsequent treatments with HNO_3 and ignitions at 550° is moistened with $HClO_4$ and heated at 550° to expel Ru. The sol. matter of the final ash is quant. extracted with HCl; to the acid soln. (25 to 35 ml, containing the equiv. of 4 ml of conc. HCl) are added CsCl (10 mg, as carrier), 0·2M-$Co(NO_3)_2$ (2 ml) and finally, after heating at 100° for 5 min., 0·2M-$K_3Co(CN)_6$ (2 ml). The ppt is separated by centrifuging, and the ^{137}Cs co-pptd. with the cobaltous cobalticyanide is determined with a well-type scintillation counter, a single-channel pulse-height analyser and a scaler. If required, the ^{90}Sr can be pptd. (with a carrier) as carbonate from the supernatant liquid or from the HCl soln. of the ash before the co-pptn. of the ^{137}Cs. The method is suitable for routine analyses. Recoveries of Cs, with ^{134}Cs as tracer, from liver or muscle tissue are ≃99%. P. S. ARUP

3850. **Determination of calcium in biological material. The use of calcein as an indicator in the EDTA titration.** T. Y. Toribara and L. Koval (Dept. of Rad. Biol., Univ. of Rochester, New York, U.S.A.). *Talanta*, 1961, **7** (3–4), 248–252 (in English).—*Procedure*—Dilute 0·5 ml of serum with H_2O (4 ml), add 4 drops of acetic acid, 1 drop of bromocresol green indicator, 4% ammonium oxalate soln. (1 ml) and conc. aq. NH_3 soln. to give a pH of 4·7 (blue - green). Cool overnight, centrifuge, and decant the liquid. Dry and heat the pptd. Ca oxalate in the tube at 500° for 1 hr. Cool, add 1 drop of HCl (1:3), 5 ml of H_2O, 1 ml of 4% KOH soln. and 0·05 ml of calcein soln. (0·004% in 0·25N-KOH). Titrate with 0·0005M-EDTA (disodium salt) under u.v. light.
P. D. PARR-RICHARD

3851. **Calcium and magnesium determination in bovine blood by EDTA titration.** G. M. Ward, R. C. Lindsay and C. A. Vair (Colorado State Univ., Fort Collins, U.S.A.). *J. Dairy Sci.*, 1960, **43** (7), 1014–1015.—The determinations may be carried out simply and rapidly by titration of the blood-serum samples with EDTA, with Cal-Red as indicator at pH 12 for Ca^{2+} and Eriochrome black T as indicator in aq. NH_3 buffer (pH 10·2), and in the presence of sodium tungstate, for Mg^{2+}. The correlation of results with those obtained by standard methods is given and discussed.
W. H. C. SHAW

3852. **Estimation of calcium and magnesium in blood serum by the cathode-ray polarograph.** E. A. Irving and P. S. Watts (Inst. of Med. and Vet. Sci., Adelaide, S. Australia). *Biochem. J.*, 1961, **79** (2), 429–432.—The sum of Ca and Mg is determined first and then the Mg alone is determined after pptn. of the Ca as oxalate; Ca is obtained by difference. The method is as accurate as, and more rapid than, available chemical methods. The results for Ca tend to be slightly higher than those obtained by chemical methods. J. N. ASHLEY

3853. **Rapid and sensitive sub-micro phosphorus determination.** C. J. F. Böttcher, C. M. van Gent and C. Pries (Leiden Univ., Netherlands). *Anal. Chim. Acta*, 1961, **24** (2), 203–204 (in English).—In the method of Bartlett (*Anal. Abstr.*, 1959, **6**, 4895) the initial digestion of the organic material with H_2SO_4 requires 4·5 hr. The digestion time is reduced to 40 min. if the sample is heated with 70% $HClO_4$ (0·2 ml) in a tube (125 mm × 15 mm) standing to a depth of 30 mm in a thermostatically controlled heating block at 180°. The liquid clears after 12 to 18 min. and is heated for a further 20 min. H. N. S.

3854. **Determination of inorganic sulphate in studies on the enzymic and non-enzymic hydrolysis of carbohydrate and other sulphate esters.** K. S. Dodgson (Dept. of Biochem., Univ. of Wales, Cardiff). *Biochem J.*, 1961, **78** (2), 312–319.—Three modifications of a turbidimetric method, differing essentially only in the scale of working, are described. The SO_4^{2-} are pptd. as $BaSO_4$ with a 0·5% aq. soln. of $BaCl_2$ containing 0·5% of gelatin, which acts as a stabiliser. The suspension is stable for at least 1 hr. and the extinction is measured in a quartz cell at 360 mμ. It can also be measured at 500 mμ (but with less sensitivity) when materials which tend to absorb u.v. light are present. The methods are simple and rapid, but are less sensitive than the benzidine or chloranilate methods. The first modification is used for the range 0 to 200 μg of SO_4^{2-} and is suitable for following the non-enzymic hydrolysis of monosaccharide sulphates by hydrazine; the second modification, which is applicable to the determination of up to 40 μg of SO_4^{2-}, is used for the assay of purified glycosulphatase preparations; the third method, which covers the range 0 to 12 μg of SO_4^{2-}, is used for the micro-analysis of various ester sulphates. The modifications can be used in the presence of hydrazine, imidazole, various buffers, anions and cations, monosaccharide mono- and di-sulphates, and some sulphate esters, but SO_3^{2-}, Ba^{2+} and $P_2O_7^{4-}$ (in concn. > 0·01M) and many polysaccharide sulphate esters interfere. J. N. Ashley

3855. **Radiochemical investigation of the behaviour of inorganic ions in gel filtration with Sephadex. Micro-determination of protein-bound iodine in blood serum.** H. Spitzy, H. Skrube and K. Müller (Chem. Abt., Paracelsus Inst., Bad Hall, Austria). *Mikrochim. Acta*, 1961, (2), 296–307 (in German).—Inorganic ions may be rapidly removed from protein soln. by gel filtration with a dextran gel, Sephadex (*cf.* Porath and Flodin, *Nature*, 1959, **183**, 1657). The behaviour of the ions depends on their concn., on the soln. used to swell the Sephadex and on the soln. used as eluent. In soln. of low ionic strength, cations are adsorbed but anions are not. On increasing the ionic strength of the eluent, both cations and anions are adsorbed by the gel, and it is possible to separate inorganic ions from proteins. For the removal of I^- from serum samples before the determination of protein-bound iodine, the sample (0·5 ml) is applied to a column (120 mm × 10 mm) of Sephadex treated with 0·9% NaCl soln. and eluted with 0·9% NaCl soln. at 0·75 ml per min.; 1-ml fractions of eluate are collected. Protein is removed quantitatively in fractions 3 to 7 and I^- in fractions 9 to 14. Twelve comparison analyses of samples containing 2 to 13 μg of protein-bound iodine per 100 ml by the gel-filtration and trichloroacetic acid pptn. methods gave results agreeing to within 5%. The gel-filtration method is particularly suitable for the analysis of serum samples containing abnormally large amounts of I^-. W. T. Carter

3856. **Micro-determination of iron in biological material with ferron.** V. Kauppinen (Dept. Biochem., Univ. Helsinki, Finland). *Suomen Kem. B*, 1961, **34**, (2), 27–29 (in English).—The method is based on the procedure of Ziegler *et al.* (*Anal. Abstr.*, 1957, **4**, 2978). In six experiments, the recovery of Fe from samples of yeast ranged from 99·5% to 103%. *Procedure*—Digest the sample (*e.g.*, 100 mg of dry yeast containing 1 to 7 μg of Fe) with conc. H_2SO_4 (1 ml) and 30% H_2O_2 soln. until clear; heat for <45 min. until decomposition of H_2O_2 is complete; cool, add H_2O (5 ml) and heat at 90° for <30 min. to decompose pyrophosphates; cool, dilute with H_2O to 5 ml and add 0·025% ferron soln. (2 ml). Treat a reagent blank and standard Fe soln. similarly. Neutralise the reagent blank with aq. NH_3 to the yellow - green colour of ferron and add the same vol. of aq. NH_3 to the other soln. Then add acetate buffer soln. (pH 4·6) (2 ml) and tri-n-butylammonium acetate (0·1 ml), extract with $CHCl_3$ (3 × 0·5 ml), dilute the combined extracts with $CHCl_3$ to 2·5 ml and measure the extinction at 610 mμ. A. R. Rogers

3857. **Determination of iron-55 and -59 in blood.** L. Hallberg and H. Brise (Dept. of Med., Univ. Göteborg, Sweden). *Int. J. Appl. Radiation and Isotopes*, 1960, **9** (1–4), 100–108.—The preparation of sources by electro-deposition is considered in detail. The sample, after preliminary treatment, is digested with H_2SO_4 and then with $HClO_4$. After the pptn. of $Fe(OH)_3$ it is dissolved in 6N-H_2SO_4, and 50% $(NH_4)_2SO_4$ soln. (2 ml) and satd. ammonium oxalate soln. (35 ml) are added. The Fe is then deposited on a copper planchette by passing a current of 0·4 amp. for 4 hr., with a platinum spiral anode at a distance of 2 cm. The planchette is washed with ethanol and counted in a gas-flow counter, first with a 0·75-mm beryllium absorber and then with a 0·011-mm platinum absorber, and the contributions from ^{55}Fe and ^{59}Fe are calculated. The recovery of Fe is ≃95%. G. J. Hunter

3858. **Simultaneous determination of ethyl ether and ethanol in blood and viscera by gas chromatography. Application to a medico-legal case.** L. Maricq and L. Molle (Lab. de Chim. Toxic., Univ. Libre de Bruxelles, Belgium). *Ann. Pharm. Franç.*, 1960, **18** (11), 811–816.—After suitable preparation, samples from blood and viscera are chromatographed on Carbowax 1500 on Celite in a 4-metre column at 106° ± 0·5°, with H as carrier gas at 25 ml per min. *Procedure*—For blood, 5 ml is pptd. with tungstophosphoric acid and, after centrifugation, 10 μl of the supernatant liquid is injected into the gas stream. For brain, 150 g of the organ is distilled with 100 ml of satd. aq. picric acid, and 50 ml is collected. This vol. is reduced to 10 ml by fractional distillation and 10 μl is injected on to the column. For stomach contents, a procedure similar to that for brain is described. E. J. H. Birch

3859. **Colorimetric determination of meprobamate.** O. D. Madsen and V. Schmidt (Centrallab., Centralsygehuset, Nyköbing, Denmark). *Ugeskr. Laeg.*, 1960, **122** (26), 891–893.—The colorimetric method of Hoffman and Ludwig (*Anal. Abstr.*, 1960, **7**, 3402) was used for the determination of meprobamate in serum or plasma, and was found to be satisfactory for clinical use, with an accuracy of 5 to 10%. The prescribed procedure must be strictly adhered to. P. Pedersen

3860. **Improved photometric method for assaying phenolsulphonephthalein in the blood of cattle in tests for renal function.** R. R. Anderson and J. P. Mixner (New Jersey Agric. Expt. Sta., Sussex, U.S.A.). *J. Dairy Sci.*, 1960, **43** (10), 1471–1475.—Errors due to free haemoglobin (**I**) in plasma samples containing phenolsulphonephthalein (**II**) are minimised by the procedure described. From a study of the extinction of samples without **11**,

but with varying degrees of induced haemolysis, a regression equation is derived from which the correction required for **I** under the basic conditions used for the photometric measurement of **II** may be calculated from the extinction in acid solution. The accuracy and precision of the method are discussed. W. H. C. SHAW

3861. **Correction for haemolysis in a photometric method for assaying sulphobromophthalein in the blood of cattle in tests for hepatic function.** R. R. Anderson and J. P. Mixner (New Jersey Agric. Expt. Sta., Sussex, U.S.A.). *J. Dairy Sci.*, 1960, **43** (10), 1465–1470.—Errors due to free haemoglobin (**I**) in plasma samples containing sulphobromophthalein (**II**) are minimised by the procedure described. From a study of the extinction of samples without **II**, but with varying degrees of induced haemolysis, a regression equation is derived from which the correction required for **I** under the basic conditions used for the photometric measurement of **II** may be calculated from the extinction in acid solution. Improved precision and accuracy are attained, but the method should be applied only when haemolysed plasma samples are to be assayed. W. H. C. SHAW

3862. **Two-dimensional system of paper chromatography of some sugar phosphates.** E. J. Wawszkiewicz (Dept. of Biochem., Univ. Calif., Berkeley, U.S.A.). *Anal. Chem.*, 1961, **33** (2), 252–254.—To prevent trailing of the phosphate esters, EDTA (ammonium salt) (pH 5) is added to each of the two solvents [7·7% ammonium acetate soln. (pH 5) - 95% ethanol (3:7), and 95% ethanol - n-butanol (32:52·5) to which is added 2 g of picric acid], and paper washed with 1% oxalic acid soln. is used. R_P data for 40 compounds are listed. G. P. COOK

3863. **Densitometric determination of aesculin and fraxin after paper electrophoresis.** G. Faugeras and R. Paris (Lab. de Mat. Méd., Fac. de Pharm., Paris). *Ann. Pharm. Franç.*, 1960, **18** (10), 698–704. —The optimum conditions for the separation of aesculin or fraxin from possible interfering substances and their subsequent determination were investigated and the following method was developed. *Procedure*—A sample of 10 μl containing 5 to 10 μg of aesculin or fraxin is placed on Arches 302 paper soaked in 0·5% sodium borate soln. Equal vol. of at least four different standard soln., with a content of pure substance between 1 and 10 μg, are also placed on the paper and the electropherogram is run for 2 to 3 hr. at 10 to 20 V per cm. The extinction of the dried strip is then determined at 365 mμ. The densitometer is first used in the direction of the electrophoresis to ensure perfect separation of the aesculin or fraxin, and then mm by mm across the strip at the level of the subject and control spots. The sums of the extinctions give a calibration curve from which the concn. in the subject spot is determined. When the spot is not sufficiently isolated, the determination is possible by constructing a curve of the variation of extinction in the spot and extrapolating when necessary, and determining the area of the peak with a planimeter. E. J. H. BIRCH

3864. **Examination of an infra-red method for determination of ratio of coproporphyrin isomers I and III.** H. L. Dinsmore and C. J. Watson (Minnesota Univ., Minneapolis, U.S.A.). *J. Lab. Clin. Med.*, 1960, **56** (4), 652–658.—The method depends on the differences in infra-red spectra (8 to 9 μ) of the solid methyl esters of coproporphyrins I and III. The proportions are calculated by a difference technique, but uncontrollable variation in the ratio of crystalline to amorphous material limits the accuracy to ≃15%. The method is inferior to fluorescence and chromatographic procedures, but is useful as an independent check and for identifications. W. H. C. SHAW

3865. **Resolution of phosphatides by chromatography on a thin film of silica gel.** W. Schlemmer (Ist. di Chim. Biol., Univ. Bologna, Italy). *Boll. Soc. Ital. Biol. Sper.*, 1961, **37** (3), 134–137.—A rapid method is briefly described. A silica-gel film (≃250 μ thick) is prepared on a sheet of glass (20 cm × 20 cm) by means of a special apparatus (Desaga, Heidelberg) and heated for 1·5 hr. at 120° before use. Successful separations of up to 250 μg of mixed phosphatides were achieved with $CHCl_3$ - methanol - water (75:22:3 or 13:6:1) as solvent. Individual phosphatides were detected by spraying with ammonium molybdate soln. (3 g in 250 ml of water plus 30 ml of N-HCl plus 15 ml of 60% $HClO_4$) and heating at 105° for 20 min. The R_F values decrease in the order neutral fats, cholesterol, free fatty acids, cardiolipin (and similar compounds), cephalin, lecithin, lysocephalin, sphingomyelin, lysolecithin and aminoacids. The sensitivity limit is from 2 to 5 μg. The method is rapid (35 min. for a 10-cm run) and is suitable for the identification of lipid mixtures or of phospatides in column eluates. E. C. APLING

3866. **Simple spectrophotometric method for the determination of urea in blood and urine.** T. K. With, T. D. Petersen and B. Petersen (Central Lab., Svendborg County Hosp., Denmark). *J. Clin. Path.*, 1961, **14** (2), 202–204.—Blood (3 ml) and 1·25% $ZnSO_4$ soln. in 0·03125N-H_2SO_4 (24 ml) are mixed and shaken to obtain complete haemolysis, and 0·75N-NaOH (3 ml) is then added. The mixture is shaken again and filtered (S. & S. No. 5893, Blauband, paper), 10 ml of the filtrate, followed by 2% *p*-dimethylaminobenzaldehyde soln. in 96% ethanol (10 ml), is transferred to a 25-ml flask, and the volume is made up with water. The extinction is read any time after 10 min. at 420 or 435 mμ. The procedure for urine is the same, but the specimen should be diluted if the urea concn. is >1000 mg per 100 ml. R. A. BRENAN

3867. **Chromatographic separation and purification of folic acid analogues.** V. T. Oliverio (Nat. Cancer Inst., Nat. Inst. Health, Bethesda, Md., U.S.A.). *Anal. Chem.*, 1961, **33** (2), 263–265.—Folic acid analogues are separated on diethylaminoethylcellulose anion-exchange columns by linear gradient elution with phosphate buffer at pH 8. The fractions are monitored with 254-mμ light and those giving peak transmittance are pooled and the absorption spectrum from 230 to 400 mμ is determined. The purity of a single compound is determined from the extinction at a given wavelength. G. P. COOK

3868. **Determination of δ-aminolaevulic acid according to Shuster.** T. Malinowska Dept. of Health Protection, Inst. of Nucl. Res., Warsaw, Poland). *Chem. Anal., Warsaw*, 1960, **5** (6), 1049–1054.—Shuster's picrate method (*Anal. Abstr.*, 1957, **4**, 219) is modified. *Procedure*—Trichloroacetic acid is added to a 0·5% homogenate of

liver (2 ml) protein is filtered off, and 0·02M-picric acid (0·3 ml) and 2·5N-NaOH (0·5 ml) are added to the filtrate. The mixture is heated in a water bath at 20° for 7 min., and 8N-HCl (1 ml) is added. After 10 min. the excess of picric acid is removed by shaking with ethyl ether (2 × 10 ml), for 2 min. and light petroleum (10 ml) for 1 min., and the extinction is measured at 420 mμ against a blank; 0·01 μmole of δ-aminolaevulic acid can be determined in 4 ml of sample. B. K.

3869. **Continuous polarographic determination of α-amino-acids.** W. J. Blaedel and J. W. Todd (Chem. Dept., Univ. Wisconsin, Madison, U.S.A.). *Anal. Chem.*, 1961, **33** (2), 205–207.—The method is based on the reaction of α-amino-acids with copper phosphate to produce an equivalent amount of Cu^{2+}, which are determined polarographically as the EDTA complex. Concn. of up to 6mM can be determined with a coeff. of 3% or variation greater for small amounts. The method was applied to the continuous measurement of ion-exchange column percolates. G. P. Cook

3870. **Quantitative chromatographic methods. VI. Improved procedure for determination of amino-compounds on paper chromatograms.** E. Tigane, E. H. M. Wade, J. T. Wong and C. S. Hanes (Dept. of Biochem., Univ. Toronto, Ontario, Canada). *Canad. J. Biochem. Physiol.*, 1961, **39** (2), 427–437.—For the detection and localisation of amino-acid spots on chromatograms, a fresh dip-reagent consisting of ninhydrin (125 mg), glacial acetic acid (25 ml), collidine (20 ml) and ethyl acetate (955 ml) is used. For quant. determination the spots are cut from the dried paper, wetted with methanolic borate buffer soln. [boric acid (18 g), 6N-aq. KOH (65 ml) and methanol (935 ml)] and dried in air at 40° to eliminate NH_3. The dried portions of paper are then treated, in an atmosphere of N, with the reagent previously described (Matheson *et al.*, *Anal. Abstr.*, 1961, **8**, 3990), to which one-tenth of its vol. of water is added, and the colour is developed by heating at 100° for 20 min. The soln. is then suitably diluted with 50% aq. ethanol and the extinction is measured at 570 mμ (440 mμ for proline and hydroxyproline). The yields of Ruhemann's purple from the paper spots of most amino-acids were found to be close to the stoicheiometric values.

VII. Isolation of amino-acids from serum and other fluids. C. K. Harris, E. Tigane and C. S. Hanes. *Ibid.*, 1961, **39** (2), 439–451.—A small-scale method, based on the use of miniature ion-exchange columns, is described. The resin used is Dowex 50 (H^+ form); about 350 mg of moist resin is suitable for treating 5 ml of serum or plasma, which is diluted 1:1 with water and adjusted to pH 2·0 to 2·5 with 8N-acetic acid. Elution is with 2N-triethylamine in 20% aq. acetone. The eluate is tested with bromocresol green, a change from yellow to yellow - green indicating the appearance of the amino-acid fractions, which may be quant. recovered in fractions of 1 to 2 ml. After evaporation to dryness over conc. H_2SO_4 *in vacuo*, the residue is dissolved in 100 μl of water and chromatographed on paper. Strongly acid compounds (*e.g.*, cysteic acid and taurine) are not recovered with the amino-acids by this procedure. With urine and some other biological fluids, ninhydrin-reacting compounds other than amino-acids may also be isolated, and may require special separation procedures. D. G. Moss

3871. **Gas chromatography of silylated amino-acids.** K. Rühlmann and W. Giesecke (Inst. f. Verfahrenstech. d. org. Chem., Leipzig). *Angew. Chem.*, 1961, **73** (3), 113.—The amino-acid salts are treated with trimethylchlorosilane, or the free amino-acids with *NN*-dialkyl-*N*-trimethylsilylamine, to yield the trimethylsilyl esters of the *N*-trimethylsilyl amino-acids, which can be separated by gas chromatography. N. E.

3872. **Ninhydrin assay in the presence of thiol [mercapto] compounds.** J. R. Whitaker (Dept. of Food Sci. and Technol., Univ. of Calif., Davis, U.S.A.). *Nature*, 1961, **189**, 662–663.—Mercapto-compounds such as cysteine, mercaptoethanol and 2,3-dimercaptopropan-1-ol interfere with the colorimetric determination of amino-acids with the ninhydrin reagent of Moore and Stein (*Anal. Abstr.*, 1955, **2**, 986). Leucine (≃ 0·2 μmole) and other amino-acids can be quant. determined if *N*-ethylmaleimide (4 μmoles) is added and if the amount of hydrindantin in the reagent is doubled. A. R. Rogers

3873. **Use of paper electrophoresis for the characterisation and determination of glycine. Applications.** J. Saint-Blancard and J. Storck (Centre de Transfusion-Réanimation de l'Armée, Clamart, Seine, France). *Ann. Pharm. Franç.*, 1960, **18** (10), 711–714.—A rapid method for separation and determination of glycine in protein hydrolysates, or in materials in which it is used for the stabilisation of γ-globulin, is described. *Procedure*—A sample containing up to 12 μg of glycine is spotted on to a sheet of Arches-302 paper (395 mm × 275 mm) together with 5 spots of standard soln. of glycine. Electrophoresis is carried out in a soln. made by making up 58 ml of glacial acetic acid and 26 ml of 25% formic acid to 2 litres with water. A voltage of 240 V is applied and the glycine migrates to the cathode. For qual. detection, the dried paper is dipped in 5% ethanolic ninhydrin made alkaline with 0·5 ml of N-aq. KOH and heated at 80° for 20 min. A table is given of the relative movement of other amino-acids. Unchanged proteins remain on the starting line. For quant. determination, the violet ninhydrin spot is extracted with 0·1% aq. $CdCl_2$ in 40% aq. methanol, and the extinction of the resulting pink soln. is measured at 505 mμ, against the slightly yellowish extract of the paper alone as blank. E. J. H. Birch

3874. **Quantitative determination of haemoglobin A_2 using paper electrophoresis.** R. N. Ibbotson and B. A. Crompton (Div. Clin. Path., Inst. Med. and Vet. Sci., Adelaide, S. Australia). *J. Clin. Path.*, 1961, **14** (2), 164–166.—The blood samples are collected, with EDTA (dipotassium salt) as anti-coagulant, haemolysed with water and toluene, and converted into carboxyhaemoglobin. Electrophoresis is carried out in vertical tanks with strips (25·5 cm × 4·0 cm) of Whatman No. 3 MM paper and tri(hydroxymethyl)methylamine buffer adjusted to pH 8·6 with boric acid. The treated samples (20 μl) are applied to the strips, which are then moistened with buffer on both sides to within 0·25 in. of the point of application. After passing a current of 225 V and 2 mA per strip for 16 hr., the strips are dried at 90° to 100°, fixed for 10 min. in fresh 10% $HgCl_2$ soln. and 10% glacial acetic acid in ethanol, re-dried, washed twice in water for 10 min. and then dried again. They are then stained for 10 min. in 1% bromophenol and 1% acetic acid in ethanol, washed several times in

0·5% acetic acid in 25% ethanol, and dried. The stained bands are cut out, and eluted with 1·5% Na_2CO_3 soln. in 50% methanol, and the extinctions of the eluates are read at 595 mμ in a spectrophotometer. R. A. BRENAN

3875. **Tris buffer for differentiation between haemoglobins C and E and separation of haemoglobins S from F and 'lepore' from A.** H. Lehmann and A. Sharih (Dept. of Path., St. Bartholomew's Hosp., London). *J. Clin. Path.*, 1961, **14** (2), 200–201.—The use of tri(hydroxymethyl)methylamine buffer in addition to the more usual barbiturate buffer in the investigation of haemoglobins is advocated. R. A. BRENAN

3876. **Rapid method for the estimation of serum haptoglobin.** D. S. Rowe (Dept. of Exp. Path., Univ. of Birmingham, England). *J. Clin. Path.*, 1961, **14** (2), 205–206.—The serum mixed with varied amounts of carboxyhaemoglobin (ranging from 0·2 to 1·6 mg per ml of serum) is placed in a series of holes in agar gel on a glass plate and subjected to electrophoresis at 240 V and 12 mA for 45 min. The plate is then placed in benzidine stain [0·2% of benzidine in 0·5% acetic acid; immediately before use, 0·2 ml of 30% (w/v) H_2O_2 soln. is added to each 100 ml]. Haptoglobin-bound haemoglobin moves slightly towards the anode and free haemoglobin towards the cathode. R. A. BRENAN

3877. **Staining lipoproteins before their separation by paper electrophoresis.** V. F. Bogoyavlenskiĭ and D. N. Rozenshtein. *Vracheb. Delo*, 1960, (8), 125–126; *Ref. Zhur., Khim., Biol. Khim.*, 1960, (6), Abstr. No. 6S84.—*Procedure*—Add Sudan I (C.I. Solvent Yellow 14) or Sudan black (C.I. Solvent Black 3) soln. (0·25 g in 100 ml of ethanol) (0·1 ml) to fresh blood serum (0·5 ml) and set it aside for 30 min. Subject the coloured serum (0·05 to 0·1 ml) to electrophoresis, and analyse the electropherogram by the usual methods. K. R. COOK

3878. **Spectrophotometric determination of nucleic acids in higher plants.** S. V. Netupskaya, Yu. V. Peruanskiĭ and V. G. Konarev. *Byull. Nuklein. Obmena u Rasteniĭ*, 1959, 148–153; *Ref. Zhur., Khim., Biol. Khim.*, 1961, (3), Abstr. No. 3S27.—Grind leaves (1 to 2 g), seeds, or starch grains as finely as possible in a soln. (5 ml) made 0·001N with respect to H_2SO_4 in 80% ethanol, dilute to 20 ml with the same soln., filter, and wash the residue with 80% ethanol, acetone, and ethanol - ether (1 : 1) to remove chlorides, free purines, pigments and most of the lipid content. Add N-H_2SO_4 (20 ml) to the residue and hydrolyse it in a boiling-water bath for 1 hr. to obtain the purines from the nucleic acids. Add 0·5N-$AgNO_3$ (1 ml) to the hydrolysate (10 ml), place the mixture in a refrigerator for 1 hr., then centrifuge, wash the residue with 0·01N-H_2SO_4 satd. with Ag_2SO_4 and dissolve it in N-HCl (1 ml). Set the soln. aside for 1 hr., centrifuge, and measure the supernatant liquid photometrically for its purine content. Maximum reproducibility is attained with a purine concn. of 4 to 12 μg per ml. K. R. COOK

3879. **Detection of ribonucleic acid with a methyl green - pyronine mixture.** R. A. Simakova. *Arkh. Patol.*, 1960, **22** (6), 81–82; *Ref. Zhur., Khim., Biol. Khim.*, 1961, (1), Abstr. No. 1S34.—The reagent normally used for the detection of ribonuclease is modified as follows—0·5% methyl green soln. (4 ml) which has been purified by extraction with $CHCl_3$ is mixed with 1% pyronine G soln. (9 ml) The soln. is diluted to 25 ml with H_2O, and acetate. buffer (pH 4·8) (25 ml) is added. The reagent is stable for a week if stored in a refrigerator. K. R. COOK

3880. **Quantitative micro-determination of cholesterol using tomatine as precipitating agent.** J. J. Kabara, J. T. McLaughlin and C. A. Riegel (Dept. of Chem., Univ. Detroit, Mich., U.S.A.). *Anal. Chem.*, 1961, **33** (2), 305–307.—Radioactive and non-radioactive cholesterol in blood and tissue samples are determined with good specificity with tomatine as the precipitating agent. Radioactive cholesterol is measured by liquid scintillation counting and the non-active material by a colorimetric method with the Liebermann - Burchard reagent. (*Cf.* Kabara, *Anal. Abstr.*, 1958, **5**, 669.) G. P. COOK

3881. **Determination of cholesterol and squalene by gas chromatography.** H. J. O'Neill and L. L. Gershbein (Armour Res. Found. of Illinois Inst. of Technol., Chicago, U.S.A.). *Anal. Chem.*, 1961, **33** (2), 182–185.—A high-temperature technique is described for determining cholesterol and squalene in scalp sebum, ovarian dermoid cysts, placental lipids, basking-shark oil, tall oil and synthetic mixtures containing squalane. The analysis is carried out at 332° on a 2-ft. column of 30% Apiezon-L grease on 30 to 60-mesh support, with a platinum-filament katharometer detector. Helium at 50 ml per min. is the carrier gas and the analysis, made on the unsaponified fraction of the sample, is complete within 10 min. Results for cholesterol on various samples containing from 2 to 24% of cholesterol show excellent agreement with results obtained by the Liebermann - Burchard colorimetric procedure, having an over-all deviation of ±0·7%. No evidence of thermal degradation is observed among any of the samples or components analysed. C. B. BAINES

3882. **An evaluation of the use of digitonin for the analysis of faecal sterols.** W. W. Wells and P. A. Mores (Biochem. Dept., School of Med., Univ. of Pittsburgh, Pa., U.S.A.). *Nature*, 1961, **189**, 483–484.—Incompleteness of pptn. of coprostanol (5β-cholestanol) digitonide in the solvents used in the procedure of Sperry and Webb (*J. Biol. Chem.*, 1950, **187**, 97) may account for some of the quantities reported as "non-3β-hydroxyl faecal sterols." The rejected washings in the Sperry and Webb procedure may contain up to 40% of the original 5β-cholestanol. Chromatographic methods of analysis are preferred (*cf.* Coleman *et al.*, *Anal. Abstr.*, 1956, **3**, 3431). A. R. ROGERS

3883. **Simplified quantitative analysis by countercurrent distribution. I. Analysis of one and of two stages.** G. Pancrazio and P. Del Grande; **II. Apparatus with lower mobile phase: analysis of binary mixtures of oestrogens.** M. Vitali, G. Sbarigia and G. Pancrazio; **III. Apparatus with two mobile phases: analysis of mixtures of corticosteroids.** G. Pancrazio and P. Del Grande (Ist. Terapeutico Romano, Rome). *Ann. Chim., Roma*, 1960, **50** (12), 1730–1752; 1753–1759; 1760–1768.—Two simplified procedures for countercurrent distribution analysis are proposed and sources of error in the determination are considered. Apparatus with a lower mobile phase or two mobile phases is described, and applications

to the analysis of binary mixtures of oestradiol and its derivatives, and of binary and ternary mixtures of corticosteroids, are shown. L. A. O'NEILL

3884. **Diagnostic preparation for the determination of serum alkaline phosphatase.** Warner-Lambert Pharmaceutical Co. Brit. Pat. 863,739; date appl. 10.7.58. U.S.A., date appl. 11.7.57.—A preparation in powder or tablet form for the determination of serum alkaline phosphatase comprises an alkali-metal or alkaline-earth-metal salt of phenolphthalein phosphate (1·5%), a magnesium salt, *e.g.*, $MgSO_4$ (0·1%), and a buffer to maintain the pH of the serum at 9 to 11, *e.g.*, tri(hydroxymethyl)methylamine (98·4%). J. M. JACOBS

3885. **Methods for the determination of some transaminase activities in biological fluids.** F. Salvatore, V. Bocchini and F. Cimino (Biochem. Dept., Univ. Naples, Italy). *Enzymologia*, 1961, **22** (6), 357–363.—A method is described for the determination of the transaminase activity of materials such as blood and cerebrospinal, ascitic, pleural and synovial fluids. Aliquots of amino-acid soln. (0·5 ml of 0·2M-L-aspartic acid or L-alanine) and 0·2 ml of 0·1M-α-oxoglutaric acid are placed in centrifuge tubes and made up to 2 ml with phosphate buffer (pH 7·4). At 37° an aliquot of the sample is added and the temp. is maintained for 10 min.; the reaction is then stopped by the addition of 50% trichloroacetic soln. (0·2 ml). With aspartic acid, 0·2 ml of fresh aniline - 80% citric acid soln. (1:1) is added to decarboxylate the oxalacetic acid formed; 1 ml of 2,4-dinitrophenylhydrazine soln. (0·1% in 2·5N-HCl) is then added and allowed to react for 5 min. at 37°. The colour is extracted with xylene (2 ml), an aliquot (1 ml) is mixed with 25% ethanolic KOH soln. (6 ml) and the extinction is measured at 490 mμ. Alanine - oxoglutaric and aspartic - oxoglutaric transaminase activities can be determined directly in blood plasma or serum, but other fluids need preliminary concentration by freeze-drying. Typical values for samples from diseased subjects are given and the technique is suggested as an aid to diagnosis. J. R. HUDSON

3886. **Assay of human plasminogen with casein as substrate.** M. Derechin (Lister Inst., Chelsea Bridge Rd., London, England). *Biochem. J.*, 1961, **78** (2), 443–448.—A triphasic graph is obtained when the proteolysis of casein by plasmin is followed by measurement of the increase in material which is sol. in $HClO_4$ and has an absorption max. at 276 mμ. Only the second part of the graph is linear. Unreliable results are obtained in the assays of plasminogen prep. based on single samples taken after a definite time of proteolysis, because of the influence of the lag period of the reaction before the linear portion of the graph is reached. The length of this lag period increases with increase in the concn. of the substrate or with decrease in enzyme concn. The slope of the linear part of the graph is proportional to enzyme activity and is practically independent of substrate concn. over a 10-fold range. A standardised procedure is described in which the proteolysis is carried out at 40° and pH 7·6. This gives reliable results when these are calculated from the slope of the linear part of the reaction graph. J. N. ASHLEY

See also Abstracts—**3561**: *Section Vb.* Products of alkali treatment of keratin. **3584**, Simultaneous estimation of nuclides. **3771**, **3772**, Titration of mercapto-groups. **3779**, Gas-chromatographic analysis of sugar mixtures. **3803**, Determination of carcinogenic hydrocarbons. **3896**, Triterpenoids and saponins in plants. **3897**, Determination of corticosteroids. **3903**, Continuous measurement of dissolved O in fermentation media. **3911**, *N*-Phthaloylglutamimide in blood. **3922**, Glycogen in oysters. **3954**, Ascorbic and dehydroascorbic acids in plants. **3959**, Amino-acids in natural water. **3978**, Automatic analysis of body fluids.

Pharmaceutical analysis

3887. **Use of anhydrous propionic acid as solvent for titration of some alkaloids.** S. Przyszlakowski (Dept. of Inorg. Chem., Med. Acad., Lublin, Poland). *Acta Polon. Pharm.*, 1960, **17** (5), 395–398.—Brucine, codeine, diamorphine, narceine, narcotine, quinine and veratrine were determined by means of potentiometric titration with $HClO_4$ in anhyd. solvents. Of the two solvents used, anhyd. acetic acid and anhyd. propionic acid, the latter was the more satisfactory, especially for the titration of weak bases with 0·01N-$HClO_4$. B. K.

3888. **The use of paper chromatography for checking methods for the determination of morphine in opium. I.** J. Büchi and R. Huber (Pharm. Inst., Eidg. Tech. Hochsch., Zürich). *Pharm. Acta Helv.*, 1961, **36** (1–2–3), 119–130 (in German).—The method of the Ph. Helv. V for the extraction of morphine from opium and some modifications have been critically examined by paper-chromatographic techniques. A. R. ROGERS

3889. **Application of gas chromatography to the determination of cocaine, arecoline and pethidine.** C. Stainier and E. Gloesener (Lab. d'Analyse des Medicaments, Univ. Liége, Belgium). *Farmaco, Ed. Prat.*, 1960, **15** (12), 721–731 (in French).—Arecoline and cocaine are methyl esters and pethidine is an ethyl ester. The application of gas chromatography to the determination of these compounds depends on the measurement of the volatile methanol and ethanol resulting from hydrolysis. Dissolve arecoline hydrobromide (50 mg) in 94% ethanol containing 3·5% KOH (1 ml) and add a known amount of benzene (5 to 10%) as an internal standard. Hydrolyse the mixture in a 10-ml stoppered flask for 1 hr. on a boiling-water bath. After cooling, take 0·02 ml for chromatography, with Carbowax 1500 and triethanolamine as stationary phase, and H as mobile phase at 70°; detection is by thermal conductivity. For cocaine, 60 to 70 mg of the hydrochloride is hydrolysed with 5% ethanolic KOH, and for pethidine, propanol is used instead of ethanol in the hydrolysis. J. I. M. JONES

3890. **Quantitative paper-chromatographic determination of alkaloids from the thorn apple (*Datura stramonium*).** N. Mešiček (Inst. Org. Chem., Univ., Ljubljana, Yugoslavia). *Mikrochim. Acta*, 1961, (2), 283–288 (in German).—Hyoscyamine and atropine can be separated from hyoscine, but not from one another, by ascending chromatography on buffered paper (pH 7·0 to 7·6) with water-saturated butanol or amyl alcohol as mobile phase. The separated alkaloids are detected by spraying the paper with Dragendorff reagent, and determined colorimetrically by extracting the excised areas from the chromatogram with acetic anhydride and

measuring the extinction at 485 mμ. The results obtained on extracts of stramonium are 40% lower than titrimetric values owing to the presence of basic substances other than alkaloids which interfere in the titration. W. T. CARTER

3891. **Determination of *N*-*p*-phenylbenzylatropinium bromide (Gastripon) and its administration forms.** Z. Jung and H. Petříková (State Inst. for Control of Drugs, Prague). *Českosl. Farm.*, 1961, **10** (2), 72–75.—The characteristic absorption of *N*-*p*-phenylbenzylatropinium bromide (**I**) (the active ingredient of Gastripon) with a max. at 257 mμ was used for the determinations in methanol (70%), in a mixture of methanol and aq. NH_3 (25%) (7:3) and in a soln. of N-HCl in methanol (70%). For the determination of **I** in tablets or injections, a preliminary separation is carried out on Dowex 50-X2. *Procedure for tablets*—Heat the powdered tablets (≃5 mg of **I**) with methanol (70%) (30 ml) in a 50-ml flask for 3 min. on a water bath with occasional shaking, cool, dilute with methanol (70%) to vol., mix, centrifuge and pass 12 ml through a column of Dowex 50-X2 (1 ml per min.); wash the column with methanol (70%) (25 ml), then heat it to 50° and elute **I** with 100 ml of N-HCl in methanol (70%) (1 ml per min.). Measure the extinction at 257 mμ and compare with a blank. The same procedure can be used for Gastripon injections containing **I** and urethane. J. ZÝKA

3892. **Use of Reinecke's salt for the assay of ipecacuanha root.** B. Kamiński and J. Wierzbowicz (Drug Res. Inst., Warsaw). *Acta Polon. Pharm.*, 1960, **17** (5), 387–393.—A method based on the separate pptn. of phenolic and non-phenolic alkaloids, and proposed for the next edition of Pharm. Polon. (*cf.* Borkowski and Frenclowa, *Ibid.*, 1956, **13**, 161, 169) was investigated. It was found that emetine reineckate is partly sol. in H_2O and emetine is partly soln. in $Ba(OH)_2$ soln., used for the separation of phenolic alkaloids. This accounts for the low accuracy of the proposed method and the non-repeatable results. B. K.

3893. **Determination of alkaloids in *Ephedra equisetina*.** R. A. Vidozminena. *Farm. Zhur.*, 1960, (3), 43–45; *Ref. Zhur., Khim., Biol. Khim.*, 1961, (6), Abstr. No. 6S94.—*Procedure*—Add 1% H_2SO_4 (100 ml) to ground *Ephedra equisetina* (10 g) and agitate the mixture for 1 hr. Filter, neutralise the filtrate to litmus with 30% NaOH soln. and extract the alkaloids with ether (30 ml, 3 × 25 ml). Combine the extracts and dry them with anhyd. Na_2SO_4, filter, and evaporate the filtrate to 3 to 5 ml; add 0·1N-HCl (20 ml) and distil off the residual ether. Titrate the uncombined HCl with 0·1N-NaOH to methyl red and calculate the alkaloid content; 1 ml of 0·1N-HCl ≡ 0·0165 g of total alkaloids. K. R. COOK

3894. **Analysis of ergot alkaloids. III. Quantitative determination of alkaloids in Secale concentratum (Stada).** M. Klavehn, H. Rochelmeyer and J. Seyfried (Pharm. Inst. der Johannes-Gutenberg-Univ., Mainz). *Dtsch. ApothZtg*, 1961, **101** (4), 75–78.—The sample, containing 0·2 to 1 mg of total alkaloid and dissolved in dichloromethane - methanol (10:1), is applied along a line 7 cm long on paper impregnated with formamide - ethanol (2:3), and chromatographed with benzene saturated with formamide or $CHCl_3$ - ethanol (19:1) for water-insol. or water-sol. alkaloids, respectively. Zones are detected by irradiation with u.v. light, then cut out and individually eluted with ethyl acetate - dimethylformamide (20:1). The ethyl acetate is evaporated, the residue is dissolved in acetic acid, and diluted with water, and the alkaloid is determined spectrophotometrically. Separation on thin films of silica gel with $CHCl_3$ - ethanol (10:1) as solvent is also described. As little as 0·1 μg of alkaloid may be detected by spraying the chromatogram with *p*-dimethylaminobenzaldehyde in HCl and drying at 105°. A. G. COOPER

3895. **Determination of reserpine. II. The nitrite method.** O. Weis-Fogh (Danmarks Apotekerforening, Copenhagen, Denmark). *Arch. Pharm. Chemi*, 1960, **67** (9), 425–443.—The method of Szalkowski and Mader (*Anal. Abstr.*, 1957, **4**, 654) and the modifications of Banes *et al.* (*Anal. Abstr.*, 1957, **4**, 1324) are critically examined, together with the influence of four antioxidants. The accuracy is somewhat less in the presence of antioxidants, but the results are reproducible to within ±2%. P. PEDERSEN

3896. **Triterpenoid compounds in plant materials. III. Paper chromatography of triterpene alcohols.** B. Pasich (Dept. of Pharmacog., Med. Acad., Poznań, Poland). *Dissert. Pharm., Krakow*, 1960, **12** (3), 201–210 (in English).—A mixture of 6 triterpenoids (aescigenin, primulagenin A, betulin, lupeol, arnidenediol and α-lactucerol) is separated by means of paper chromatography. The R_F values of the components on Whatman No. 1 paper, impregnated with aluminium hydroxide, in such solvents as benzene, cyclohexane, toluene and xylene, are given, and colour reactions with 8 reagents are tabulated. Triterpenoid compounds are detectable on chromatograms in amounts of 5 to 10 μg per sq. cm, and identification is possible, by comparison with standards, of 25 to 50 μg per sq. cm.

IV. Chromatographic characterisation of the more important saponins in medicinal plants. B. Pasich. *Ibid.*, 1961, **13** (1), 1–10 (in English).—Saponins isolated from the seeds of *Aesculus hippocastanum* L. (**I**), the roots and rhizomes of *Saponaria officinalis* L. (**II**), the roots of *Gypsophila paniculata* Fisch. (**III**), the roots and rhizomes of *Primula officinalis* L. (**IV**), the flowers of *Calendula officinalis* L. (**V**), the bark of *Quillaia saponaria* Molina (**VI**), the roots and rhizomes of *Polygala senga* L. (**VII**), and *Herniaria glabra* L. herb (**VIII**) were investigated chromatographically. Three solvent systems were used, the best results being given with n-butanol - acetic acid - H_2O (6:1:3), with the ascending technique, for 15 hr. The saponin spots were revealed with 5 colour reactions and 2 haemolytic tests. The reaction with alcoholic tungstophosphoric acid soln. was the most valuable for the identification. The limit of detection is from 5 to 40 μg. R_F values and colours of the spots in daylight and u.v. with the various reagents are tabulated. It was found that the saponin of **V** contains three triterpenoid glycosides, and the saponins of **II**, **III**, **VI**, **VII** and **VIII** each contain two components. Aescinol (obtained from **I**) and primulic acid (from **IV**) each contains only one triterpenoid component. B. K.

3897. **Determination of corticosteroids in their pharmaceutical forms by means of *p*-nitrosodimethylaniline.** J. Verdier (Centre de Rech., Roussel-Uclaf, Paris, France). *Ann. Pharm. Franç.*, 1960, **18** (11), 795–799.—The speed of

reaction of a number of corticosteroids with *p*-nitrosodimethylaniline is determined with a view to the application of the Pesez reaction (*cf.* Pesez and Robin, *Ibid.*, 1959, **17**, 624). *Procedure*—With the more rapidly reacting compounds, add to 1 ml of the ethanolic soln. of the steroid (obtained by procedures which are outlined) 0·5 ml of 0·1% ethanolic *p*-nitrosodimethylaniline and then, after 5 min. at 0°, 0·5 ml of 0·1N-NaOH. After setting the mixture aside for 1 to 6 hr. (a table of times for various compounds is given) in the absence of light, at 0°, add 2 ml of borate buffer (pH 9·8), 5 ml of 0·1% ethanolic phenol and 0·5 ml of fresh aq. $K_3Fe(CN)_6$, and after 10 min. at 20° ± 2° measure the extinction at 650 mμ. With the less rapidly reacting steroids (hemisuccinic, cyclohexanecarboxylic or *m*-sulphobenzoic esters), add to 1 ml of the steroid soln. 1 ml of the *p*-nitrosodimethylaniline soln. and, after 5 min. at room temp. (25°), 1 ml of 0·1N-NaOH. After 1 to 2 hr. at room temp., shaded from the light, complete the determination as described above. E. J. H. Birch

3898. **Simplifications of the colorimetric hydroxylamine method for penicillin determination in fermentation media and finished salts.** L. Carta-de Angeli, M. T. Ventura and F. Dentice di Accadia (Ist. Sup. San., Centro Int. di Chimica Microbiol., Roma, Italy). *R.C. Ist. Sup. Sanit.*, 1960, **23** (10–11), 915–923.—Penicillin is determined by reaction with a neutralised ethanolic soln. of hydroxyammonium chloride and a 20% soln. of $(NH_4)_2SO_4.Fe_2(SO_4)_3$. The procedure is applicable to an aq. or ethanolic soln. of salts or to the n-butanol extract from fermentation media, previously adjusted to pH 2. A blank is not necessary except with highly coloured extracts, when a dulpicate extract, inactivated by boiling for 5 min. after acidification to pH 2, is satisfactory. The method is reproducible to within ± 2%, and is recommended for routine analyses.

E. C. Apling

3899. **Determination of tetracycline and chlortetracycline when present together.** E. N. Druzhinina. *Antibiotiki*, 1961, **6** (2), 167–172.—The cup-plate method is proposed for the determination of tetracycline (**I**) and chlortetracycline (**II**) in medicinal preparations and in *Actinomyces aureofaciens* culture fluids. The principle of the method is to determine the total activity (expressed in units of **I**) and to destroy **II** so that **I** can be determined alone; **II**, calculated by difference, is expressed in units of **I**. To determine **I**, use a medium (pH 8 to 8·2) consisting of 1 to 1·5% agar containing 135 mg of amino-N per 100 ml and 1% of glucose. Add the test culture of a spore-forming bacillus (*e.g. Bacillus subtilis*) (30 to 40 million organisms per ml of medium) to the medium at 65° to 70° and add 10 ml of the seeded medium to each cup. Dissolve dry test samples in 0·01N-HCl to obtain a concn. of 1 mg per ml. Dilute culture fluids and test soln. in NaOH - citrate buffer (pH 7·8 to 8) to ≃2 units of **I** per ml. Prepare standard soln. of 2 units of **I** per ml in the same buffer. To determine the total activity of **I** plus **II** in comparison with standard **I** soln. dilute all test and standard soln. in an HCl - citrate buffer (pH 3 to 3·2); use the same agar medium as before but at neutral pH. Tabulated results for culture fluids and dry samples by the spectrophotometric method are in good agreement with the results obtained by this method; it is possible to control fermentation and the various stages of purification with the same precision as with the spectrophotometric method.

K. R. Cook

3900. **Simplified spectrophotometric assay of griseofulvin in fermentation samples.** C. Daly (Glaxo Lab. Ltd., Ulverston, Lancs., England). *Analyst*, 1961, **86**, 129–131.—At 7 equally spaced wavelengths (288, 290 . . . 300 mμ) the extinctions of a standard soln. of griseofulvin in butyl acetate and of the sample in the same solvent are measured for all but the middle wavelength. Hence by a simple equation the proportion of griseofulvin in the sample is calculated. The method is similar in principle to that of Ashton *et al.* (*Ibid.*, 1956, **81**, 220, 225), but avoids complex calculations and has the advantage that the standards may be set up at the same time as the sample. A. O. Jones

3901. **Differential assay for mitomycin A and C.** A. Gourevitch, V. Z. Rossomano and J. Lein (Bristol Lab., Syracuse, N.Y., U.S.A.). *Antibiot. & Chemother.*, 1961, **11** (1), 48–51.—The method is based on the observation that mitomycin A has 20 times the activity of mitomycin C against *Bacillus subtilis* ATCC 6633, whereas the two antibiotics have identical activities against *Klebsiella pneumoniae* FDA 602. In the agar-diffusion assays described, dose - response curves with *B. subtilis* are linear and parallel with 0·4 to 10 and 0·001 to 0·02 μg per ml, respectively. With *K. pneumoniae*, the linear range for each antibiotic is 0·5 to 60 μg per ml. Results are read off from a nomogram.

W. H. C. Shaw

3902. **Adaptation of the Quebec colony-counter for antibiotic zone reading.** N. Grecz (Chicago Univ., Ill., U.S.A.). *Antibiot. & Chemother.*, 1961, **11** (1), 46–47.—A description is given of the preparation and use of a simple inexpensive transparent measuring scale made from commercial (U.S.) cross-hatched acetate sheet.

W. H. C. Shaw

3903. **Continuous measurement of dissolved oxygen in fermentation media in the presence of micro-organisms.** G. Gualandi, G. Morisi, G. Ugolini and E. B. Chain (Ist. Sup. San., Centro Int. di Chim. Microbiol., Roma, Italy). *R.C. Ist. Sup. Sanit.*, 1960, **23** (10–11), 822–868.—The construction and use of two specially designed amalgamated silver electrode systems is described, and detailed constructional diagrams are given. The first system, suitable for semi-continuous measurements in shake-flasks or in fermentation vessels, consists of a disc anode (20 mm × 1·5 mm) and a silver-wire cathode, set into a cylinder of epoxide resin (Araldite D), covered with a film of collodion (≃0·3 μ), and sterilised by immersion in 15% formaldehyde soln. for 30 min. Equilibration of the electrodes with the soln. takes several minutes, but the sensitivity remains constant if current is passed for ⩾ 60 sec. at intervals of ⩽ 20 min. In the second system, designed for continuous measurements in large fermenting vessels, a wire microcathode, the surface of which is continuously cleansed by means of a velvet-covered rotating disc, is used. The electrode system forms a compact unit which will withstand sterilisation by steam at 125° for 60 min. The two systems give comparable results when used to measure dissolved oxygen during the course of a variety of fermentations under turbulent conditions. E. C. Apling

3904. **Analysis and production-monitoring methods and apparatus [for antibiotics].** Technicon International, Ltd. Brit. Pat. 865,251; date appl. 8.7.58. U.S.A., date appl. 23.8.57.—Apparatus and methods for monitoring the culture phase and the harvesting phase in antibiotic production by dialysis and colorimetry are claimed. J. M. JACOBS

3905. **Determination of acetylsalicylic acid and *p*-acetamidophenol associated in a tabletted preparation.** M. Mouton and M. Masson (Lab. Laroche-Navarron, Leuville-sur-Orge, Seine-et-Oise, France). *Ann. Pharm. Franç.*, 1960, **18** (10), 759–762.—*p*-Acetamidophenol (**I**) interferes in the Lautemann's red determination of acetylsalicylic acid (**II**) and a procedure which takes this into account is described. *Procedure for* **II**—An aliquot part of 5 ground tablets is extracted several times with ether to give 100 ml of filtrate, which is then extracted with 2% $NaHCO_3$ soln. (4 × 25 ml). The aq. layer is warmed to drive off ether, 4 ml of NaOH soln. (*d* 1·33) is added, and the soln. is heated on a boiling-water bath for 15 min. Conc. iodine soln. is added until starch paper is turned blue, and the soln. is heated on a boiling-water bath for 1 hr. After cooling the mixture and removal of excess of iodine with 2% Na_2SO_3, the pptd. Lautemann's red is filtered off and weighed. The excess found in a trial with known equal amounts of **I** and **II** is considered to be due to 2% of **I** still contaminating the **II**. *For* **I**—An aliquot from 5 ground tablets is extracted with 40 ml of cold methanol and filtered, and the solvent is removed by distillation. The residue is then taken up in 35 ml of 15% trichloroacetic acid soln., heated for 45 min. to hydrolyse it, and made up to 50 ml with the trichloroacetic acid soln. Standard soln. are similarly prepared. To five tubes are added standard or sample soln. and one is left as blank. Each is made up to 5 ml with 15% trichloroacetic acid soln. and 1 ml of 0·5% $NaNO_2$ soln. is added; after mixing, the soln. is left for 1 min., then 1 ml of 0·5% ammonium sulphamate soln. is added and, after mixing, the soln. is again left for 1 min. Tréfouel reagent (0·05 g of *N'*-diethyl-*N*-1-naphthylpropylendiamine in 50 ml of water (2 ml) and amyl alcohol (10 ml) are added and the colour is allowed to develop for 30 min. A 1-ml aliquot of the org. layer is diluted with amyl alcohol to 10 ml, and after 10 min. the extinction is determined at 590 mμ. E. J. H. BIRCH

3906. **Determination of piperazine salts in pharmaceutical liquids.** R. E. Pankratz (Fort Dodge Lab., Iowa, U.S.A.). *J. Pharm. Sci.*, 1961, **50** (2), 175–177.—*Procedure*—Mix the aq. soln. (5 ml containing ≮2·5 mg of piperazine base or an equiv. amount of salt) with 3% citric acid monohydrate soln. (5 ml) and freshly prepared 3% ammonium reineckate soln. (5 ml), cool in ice water for 1 hr., centrifuge, wash the ppt. with 0·009% ammonium reineckate soln. (1 ml), centrifuge and allow the ppt. to drain in the inverted tube. Dissolve the ppt. in acetone (10 ml), clarify the soln. by centrifuging and measure the extinction at 525 mμ (*cf.* Bandel, *Anal. Abstr.*, 1959, **6**, 338). If the sample contains quaternary ammonium salts that form reineckates insol. in acid soln. but soluble in alkaline soln., use satd. aq. borax soln. in place of the citric acid soln. (*cf.* Kamath *et al.*, *Anal. Abstr.*, 1958, **5**, 3140). Control of pH is important because the reineckate formed in acid soln. has an extinction double that of the reineckate formed in alkaline soln. The mean error is ± 1%. A. R. ROGERS

3907. **Determination of Phenergan [promethazine].** P. Spacu and E. Antonescu (Centre of Chem. Res., Acad. R.P.R., Bucharest). *Rev. Chim., Acad. R.P.R.*, 1960, **5** (2), 243–250 (in English).—Promethazine (15 to 50 mg) can be determined gravimetrically by pptn. of the reineckate or the hexathiocyanatochromate[III] derivative from dil. acetic acid soln.; the mean error is <50 μg. As little as 0·5 mg of promethazine can be determined gravimetrically as the reineckate with a mean error of <10 μg. Alternatively, the ppt. of the hexathiocyanatochromate can be dissolved in acetone and determined by potentiometric titration with 0·05N-$AgNO_3$ (silver and satd. calomel electrodes), or absorptiometrically at 574 mμ. A. R. ROGERS

3908. **Spectrophotometric determination of naphazoline.** J. Kráčmarová and J. Kráčmar (State Inst. for Control of Drugs, Prague). *Českosl. Farm.*, 1961, **10** (2), 83–85.—*Procedure*—Dilute the sample (4 ml of 0·1% or 8 ml of 0·05% soln.) in a separating-funnel with H_2O to 25 ml, and add NaOH soln. (20%) (5 ml) and $CHCl_3$ (20 ml exactly). Shake the mixture for 10 min., then set it aside for 30 min. Filter the $CHCl_3$ layer through paper into a 25-ml burette. Evaporate 10 ml of the filtrate to dryness on a water bath, dissolve the residue in 3N-HCl (3·3 ml), dilute the soln. to 100 ml with H_2O, and filter through paper. Discard the first 10 ml and measure the extinction of another aliquot in 0·1N-HCl at 281 mμ. Compare with that of a standard soln. J. ZÝKA

3909. **Polarographic method for determination of metronidazole [Flagyl].** A. Danek (Dept. of Inorg. and Anal. Chem., Med. Acad., Krakow, Poland). *Dissert. Pharm., Krakow*, 1961, **13** (1), 107–110.—*Procedure*—To the soln. of metronidazole (5 mg in 5 ml of H_2O) add satd. KCl soln. (2·5 ml), 0·5% gelatin soln. (2 ml) and buffer (pH 2·36) up to 50 ml. Remove O from an aliquot by a stream of N and record the polarogram; the $E_{\frac{1}{2}}$ *vs.* the S.C.E. = ≃ −0·24 V. Determine a standard soln. by the same procedure. The method was used for determination of metronidazole in pure substance and in tablets. B. K.

3910. **Photometric determination of Ronicol [nicotinyl alcohol], Trafuril [tetrahydrofurfuryl nicotinate] and Cholamid [nicotinamidomethanol] by means of molybdophosphoric acid.** M. Smaga and T. Pelczar (Dept. of Inorg. and Anal. Chem., Med. Acad., Krakow, Poland). *Dissert. Pharm., Krakow*, 1960, **12** (4), 275–280.—*Procedure*—Nicotinyl alcohol and tetrahydrofurfuryl nicotinate are diluted with H_2O, and nicotinamidomethanol is dissolved in H_2O. These soln. are acidified with conc. HCl and heated to 90°, and satd. molybdophosphoric acid soln. is added. After cooling, the ppt. are collected in glass filters, washed with dil. HCl and dissolved in 0·1N-NaOH. Ammonium molybdate in H_2SO_4 is added, followed by ascorbic acid, and the soln. are boiled for 1 min. The extinctions of the cooled soln. are measured at 700 mμ, with 1-cm cells. The accuracy is ± 3%. Best results are given when the concn. of test material in the final soln. is 4 to 22 mg. B. K.

3911. **Determination and detection of *N*-phthaloylglutamimide (Thalidomide).** R. Beckmann and H. H. Kampf (Biochemische und Analytische Abteilung der Chemie Grünenthal G.m.b.H., Stolberg/Rheinland). *Arzneimittel-Forsch.*, 1961, **11**(1),

45–47.—Thalidomide (**I**) is converted in alkaline media into a phthalamic acid, with a corresponding change in the absorption curve. To determine **I** in blood, extract heparinised blood (10 ml) into $CHCl_3$ (3 × 40 ml), combine and filter the extracts and evaporate to dryness. Heat the residue twice with 0·1N-HCl (4 ml), filter and measure the extinction (E_2) at 220 mμ against 0·1N-HCl. Add N-NaOH (0·5 ml) to the test and blank soln. and read the extinction (E_1) at 220 mμ after 10 min. Deduct the blank value from the mean value of E_2–E_1 from 2 measurements and determine **I** by reference to a standard curve. Recoveries of **I** added to blood (0·5 to 2 μg per ml) were 80 to 112%. To determine **I** in non-biological fluids, evaporate the sample to dryness, add 1 ml of hydroxylamine soln. [dissolve hydroxyammonium chloride (2 g) in water (2·5 ml) and dilute to 50 ml with ethanol; dissolve NaOH (4 g) in water (2·5 ml), dilute to 50 ml with ethanol; mix equal vol. of the two soln. and centrifuge] and 2·5 ml of $Fe(ClO_4)_3$ soln. [dissolve iron wire (0·8 g) in 70% $HClO_4$ (10 ml), dilute to 100 ml with ethanol and store on ice; mix 4 ml with 70% $HClO_4$ (3·5 ml) and dilute with ethanol to 100 ml]. Measure the extinction at 530 mμ after 15 min. **I** may be identified by paper chromatography with dimethylformamide - methanol - water (5:14:1) (R_F = 0·83) and by the ferric hydroxamate test. This reaction, the resorcinol-fusion test and Zwikker's reaction (*Pharm. Weekbl.*, 1930, **68**, 975; 1931, **69**, 1178) are used to distinguish between **I** and barbitone, cyclobarbitone, hexobarbitone, phenobarbitone and methyprylone.

A. G. COOPER

3912. **Determination of arsenic valence by microbiological assay.** H. W. Loy, S. S. Schiaffino and W. B. Savchuck (Food and Drug Admin., U.S. Dept. Health, Educ., and Welfare, Washington, D.C.). *Anal. Chem.*, 1961, **33** (2), 283–285.—Microbiological assay methods were used to study the influence of a variety of arsenicals on the growth of the test organism *Lactobacillus leichmannii*. Growth inhibition decreased in the order arsenite, arsenosobenzene and arsphenamines, arsonate and nitrophenylarsonic acids, arsanilic acid. The results were used to devise a method for distinguishing ter- and quinque-valent As.

G. P. COOK

3913. **Detection of some long acting sulphonamides.** I. Tschudi-Steiner and G. Tranow (Pharm. Anstalt, Univ. Basel). *Pharm. Acta Helv.*, 1961, **36** (1–2–3), 181–185 (in German).—Sulphamethoxypyridazine (**I**), sulphadimethoxine (**II**), sulphaphenazole (**III**) and sulphamethyldiazine (**IV**) can be identified by fluorescence microscopy of the crystalline Schiff's bases produced by reaction with *p*-dimethylaminobenzaldehyde (for **I** and **III**), 2,4-dihydroxybenzaldehyde (for **I**), anisaldehyde (for **II**), veratraldehyde (for **II**), salicylaldehyde (for **IV**) and 2-naphthaldehyde (for **IV**).

A. R. ROGERS

3914. **Spectrophotometric determination of thiomersalate.** A. R. Neurath (Bioveta, Nitra, Czechoslovakia). *Českosl. Farm.*, 1961, **10** (2), 75–78.—*Procedure*—To 50 ml of a mixture (1:1) of 2N-acetic acid and 2N-H_2SO_4 add the sample (1 ml) and toluene (16 ml). Shake for 1 min. in a separating-funnel, then separate the organic layer, and to 8 ml add dithizone soln. (250μM in $CHCl_3$) (1 ml) and 1 ml of a mixture (1:1) of 2N-acetic acid and 2N-H_2SO_4; shake, and measure the extinction of the organic layer at 620 mμ. Prepare standards (0·2 to 0·8 ml of 250 μM-thiomersalate) and treat in the same way.

J. ZÝKA

3915. **Determination of Chinosol based on the formation of chelates with tervalent iron.** A. R. Neurath (Bioveta, Nitra, Czechoslovakia). *Českosl. Farm.*, 1961, **10** (2), 78–81.—The composition of the chelates of Fe^{3+} with Chinosol (**I**) was studied with the use of the Job photometric method, and a procedure was developed for the determination of **I** (> 0·1%) in serum. Mix the sample (2 ml) with ethanol (96%) (7 ml), centrifuge off the pptd. proteins, transfer the supernatant liquid to a 25-ml flask, centrifuge the residue with ethanol (3 ml), and combine the supernatant liquids. Add M-$FeCl_3$ (1 ml), dilute to vol. with buffer soln. (pH 3·29), filter, and measure the extinction at 620 mμ.

J. ZÝKA

3916. **Paper-chromatographic detection of warfarin in biological material.** Z. Stránský (State Sci. Veterinary Inst., Olomouc, Czechoslovakia). *Českosl. Farm.*, 1961, **10** (2), 81–83.—The sample is extracted with acetone (4 × 75 ml) (3 hr. per extraction), and the extract is evaporated on a water bath. The residue is dissolved in 0·1N- or 0·025N-NaOH, and filtered, and the filtrate is acidified with HCl (10%). The soln. is extracted with $CHCl_3$ (4 × 20 ml) and evaporated. The acetyl group of the isolated warfarin (**I**) is detected with a soln. of hypobromite and pyridine in alkaline medium. The isolated **I** is treated with a nitration mixture (2 ml) at 0° and the separated nitro-derivative is filtered off, dissolved in acetone and chromatographed on Whatman No. 1 paper impregnated with a 20% soln. of formamide in ethanol, with (*i*) ethanol - aq. NH_3 - H_2O (5:1:4), (*ii*) isoamyl alcohol saturated with 10% aq. NH_3 - ethanol - conc. aq. NH_3 (5:5:2), and (*iii*) CCl_4 - acetic acid (25:1) as solvents.

J. ZÝKA

3917. **Chemical determination of the adrenaline and noradrenaline content of local anaesthetics.** H. Hellberg (Chem. Dept., State Pharm. Lab., Stockholm, Sweden). *Svensk Farm. Tidskr.*, 1960, **64** (18), 493–505 (in English).—Various types of chemical methods are discussed. Fluorescence methods are preferred because of their high specificity, although they are complicated and the analytical values are relatively scattered. A statistical analysis of various factors influencing the accuracy of the 6,7-dihydroxyindoxyl method is described. Detailed instructions are given for the application of this method, both directly and in combination with separation on alumina.

P. PEDERSEN

3918. **Comments concerning the method of the Danish Pharmacopoeia for the determination of solutions of sodium citrate for blood transfusion.** F. F. Jensen (State Hosp. Pharmacy, Copenhagen, Denmark). *Arch. Pharm. Chemi*, 1960, **67** (2), 29–34.—Sodium citrate soln. are evaporated to dryness and dried to constant weight at 105°. If the evaporation is carried out to complete dryness this method gives correct results when calculated as Na citrate dihydrate; if the evaporation is not complete, the result will be about 10% low, and the substance formed is Na citrate having a lower content of water of crystallisation.

P. PEDERSEN

See also Abstracts—**3560**: *Section II*, Backscattering of β-radiation in pharm. analysis. *Section IV*, Determination of penicillin. **3561**: *Section Vb*, Polarography of vincamine. *Section VIIa*, Spectrophotometry in manufacture of oxytetracycline. **3770**, Sulphur in pharm. prpn. **3796**, Non-aq. titration of thiocompounds. **3798**, Determination of allylthiourea and allyl thiocyanate. **3827**, Chromatography of peppermint oil. **3859**, Meprobamate in blood. **3927**, Antibiotics in milk. **3952**, Assay of panthenol. **3972**, Reserpine in feeding-stuffs. **3973**, Streptomycin in feeding-stuffs. **4011**, I.r. spectra of antibiotics.

Food

Food and food additives, beverages, edible oils and fats, vitamins.

3919. **Modified molybdenum blue method for determining small amounts of arsenic [in food and food additives].** K. Bauer (Central Inst. Hygiene, Zagreb, Yugoslavia). *Kem. u Ind., Zagreb*, 1960, **9** (9), 235–238.—The quantitative method described is based on an earlier procedure (*cf.* E. B. Sandell, "Colorimetric Determination of Traces of Metals," Interscience Publ., New York, 1950), but with the reducing agent replaced by a reagent containing Mo^{6+} and Mo^{5+} (*cf.* Lucena-Conde and Prat Perez, *Anal. Abstr.*, 1957, **4**, 3911). The method can be used with org. and inorg. samples, 1 to 3 g dry wt., containing 0·3 to 10·0 μg of As per g. With org. samples, preliminary decomposition in H_2SO_4 and H_2O_2 (or H_2SO_4 and HNO_3) is required. The AsH_3, produced as in the Gutzeit method, is absorbed in 1 ml of 1·5% aq. $HgCl_2$ and 0·15 ml of 0·1% aq. $KMnO_4$. The molybdenum reagent (0·15 ml) (*loc. cit.*) is added to the test-tube, and the molybdenum blue colour is developed by heating the test-tube in boiling water. The soln. is diluted with 5 ml of H_2O and the extinction is determined at 840 mμ, and referred to a calibration curve. Large amounts of heavy metals, if present in the inorg. samples, tend to lower the results. A. L. GROCHOWSKI

3920. **Refractive index of sucrose solutions: A statistical appraisal.** S. Hill and W. J. H. Orchard (Tate & Lyle Res. Lab., Keston, Kent, England). *Int. Sugar. J.*, 1961, **63**, 42–44.—A revised refractive index table for soln. containing 54 to 81% of sucrose has been prepared from data published by Snyder (*Proc. 12th Session ICUMSA*, 1958, 23) and Charles (*Int. Sugar J.*, 1959, **61**, 236). The table is calculated from the equation—

$$S = -11261{\cdot}83664 + 21527{\cdot}00940\,n - 13828{\cdot}96545\,n^2 + 3013{\cdot}36184n^3,$$

where S is the percentage of sucrose (w/w in air) and n is the refractive index at 20°. In the regression equation, derived from the combined data, it has been assumed that n is measured without error. B. J. WALBY

3921. **Improved method for detection and approximate estimation of fungal amylase supplementation of wheat flour.** K. J. Hayden (Novadel Ltd., St. Ann's Crescent, London, S.W.18). *J. Sci. Food Agric.*, 1961, **12** (2), 123–127.—Under specified conditions of pH, treatment of flour extracts with bentonite in the presence of acetate ions results in inactivation of cereal α- and β-amylases, but has very little effect on fungal enzymes. A suspension of bentonite (20 g) in N-Na acetate (50 ml), N-HCl (15 ml) and water (35 ml) is mixed with a dispersion of powdered agar (5 g) and starch (2 g) in water (150 ml) to give a substrate buffered at pH 4·9 to 5·0. Plates are prepared and cups (4 mm deep and 7 mm in diam.) are cut in them. Samples are prepared by mixing flour (6 g) with water (10 ml) and after 5 min. the suspensions are transferred to the cups and incubated overnight at 35° to 40°. The plates are developed by flooding with 0·001 to 0·005N-iodine in 0·5% KI soln. and washed. By including standards and comparing zone diameters, treatments of 0·25, 0·5 and 1 oz per sack can be readily differentiated and as little as 0·0625 oz of fungal amylase per sack can be detected. J. R. HUDSON

3922. **Determination of glycogen in oysters.** J. R. Fraser and D. C. Holmes (D.S.I.R., Lab. of the Gov. Chemist, Clement's Inn Passage, Strand, London). *Analyst*, 1961, **86**, 131–132.—Glycogen from comminuted oyster meat can be dispersed in a soln. of $CaCl_2$ (sp. gr. 1·3 and pH 2·3) and can be determined polarimetrically ($[\alpha]_D = +203°$) by the procedures previously described for determining starch in wheat flour (Fraser *et al.*, *J. Sci. Food Agric.*, 1956, **7**, 577) and sausage meat (Fraser and Holmes, *Analyst*, 1958, **83**, 371), except that a sample wt. of 10 g is used and that 5-ml portions of Carrez's soln. (I and II) are used for pptg. sol. proteins. If P is the optical rotation of the dispersion at 20° in a 20-cm tube, the glycogen present (%) is $10^4P/406w$, where w is the sample wt. (g). When a saccharimeter is used, this result is multiplied by 0·3462. For confirmation, the filtered dispersion (50 ml) may be heated under reflux with 3 ml of conc. HCl for 1 hr., the cooled liquid diluted to 100 ml with $CaCl_2$ soln., and its optical rotation (R) measured in a 20-cm tube at 20°. The glycogen present (%) is then $10^4(P - 2R)/300\,w$. Alternatively, an aliquot of the hydrolysed dispersion may be de-calcified by passage through an ion-exchange resin (Amberlite IR-120, Na^+ form) and the reducing matter determined as glucose; then glycogen = glucose × 0·9. A. O. JONES

3923. **Reduction test for quality determination of milk. I. Mechanism of methylene blue reduction.** M. Busse (Bacteriologischen Inst. der Südd. Versuchs- u. Forschungsanst. f. Milchwirtschaft, Weihenstephan, Germany). *Z. Lebensmitt Untersuch.*, 1960, **113** (6), 453–464.—The rates of acid formation and of methylene blue reduction by resting cultures of *Streptococcus lactis*, *Strep. diacetilactis*, *Lactobacillus bulgaricus*, *Lb. casei*, *Leuconostoc mesenteroides* and *Leuc. citrovorum* were measured. The concentration of methylene blue was raised from 0·01 μmole per ml to 0·5 to 3·0 μmole per ml and acetate-buffered glucose soln. (pH 6·6) was used as medium. The ratio of the rates of acid formation to methylene blue reduction remained constant although the physiological activity of the cells declined sharply during the experiment. A detailed discussion of the mechanism of glucose breakdown is given.

II. The specific reducing power of various bacteria. M. Busse. *Ibid.*, 1960, **113** (6), 464–479.—The reducing powers of various bacteria were measured in media optimum for growth. The specific reducing power (μg of methylene blue per hr. per 10^6 cells) of *Escherichia coli* is considerably less than that of *Strep. lactis*. With *E. coli* the reducing

power decreases during the growth period, especially at the point of change into the logarithmic phase, while with *Strep. lactis* the decrease is less. With *E. coli* and at concn. of dye such that the colour is still visible a decrease in the rate of reduction to a small proportion of the max. value is observed, but with *Strep. lactis* the colour is discharged at almost constant rate. In a mixture of the two organisms, only the streptococcus is decisive for the reduction time of methylene blue.

S.C.I. Abstr.

3924. **Milk phosphatases. Determination of phosphomonoesterases in raw milk.** F. Kiermeier and E. Meinl (Milchwirtschafte. Inst. d. Tech. Hochsch., München in Weihenstephan, Germany). *Z. Lebensmittl Untersuch.*, 1961, **114** (2), 110–127.—The relevant literature is reviewed. For alkaline phosphatase the method of Sanders and Sager (*J. Dairy Sci.*, 1946, **29**, 737; 1947, **30**, 909) is critically examined for the effects of the amount of sample, the duration of heating for inactivation, the concn. of colour reagent, temp. of reaction, substrate concn. and reaction time; for acid phosphatase, factors affecting the method of Hakansson and Sjöström (*Svenska Mejeritidn.*, 1952, **44**, 15) are studied, including inhibitory substances in the substrate, autohydrolysis, the influence of light, the optimum substrate concn., reaction temp., buffer system, pH and reaction time. Details are given of modified methods. 67 references.) S.C.I. Abstr.

3925. **Correlation and relative precision of two methods of measuring the chloride content of milk.** D. H. Kleyn, C. J. Wilcox and W. A. Krienke (Florida Univ., Gainesville, U.S.A.). *J. Dairy Sci.*, 1960, **43** (10), 1505–1506.—From a statistical comparison of results obtained by a modification of Mohr's method for Cl^- in milk with those of a potentiometric method (*cf.* Herrington and Kleyn, *Anal. Abstr.*, 1961, **8**, 2143), it is concluded that the two methods are of similar precision, but that the potentiometric end-point is easier to detect. The effects of breed of cow, age, stage of lactation and season are discussed. W. H. C. Shaw

3926. **Measurement of non-ionic iodine in the milk of dairy cows following oral administration of labelled sodium iodide.** A. Morgan (A.E.R.E., Harwell, Berks., England). *J. Dairy Res.*, 1960, **27** (3), 399.—The milk samples are passed through a column of De-Acidite FF (Cl^- form) for removal of $^{131}I^-$, and the non-ionic ^{131}I in the percolate is counted in a well-type scintillation counter. The proportion of non-ionic to total ^{131}I varied from 1·2 to 14·5% in different cows. W. H. C. Shaw

3927. **An approach to a rapid test for antibiotics in milk.** H. E. Kennedy and W. J. Harper (Ohio State Univ., Columbus, U.S.A.). *J. Dairy Sci.*, 1960, **43** (7), 999–1000.—The method described is based on the bacterial reduction of 2,3,5-triphenyltetrazolium chloride (**I**) and can be used for the detection of 0·1 μg or more of terramycin per ml of milk. A fresh 5-hr. culture of *Streptococcus cremoris*, Strain 806 (0·1 ml), is placed on a 0·5-in. filter-paper disc in a Petri dish. A dry disc is placed on each inoculated disc and 0·15 ml of milk sample is added for complete saturation of both discs. After incubation for 10 min. at 30°, the upper disc is removed, one drop of 0·25% aq. **I** is added, the disc is replaced, and incubation is continued. A pink colour appears in antibiotic-free controls in about 10 min., but with samples containing 0·1 to 1·0 μg of terramycin per ml, 15 to 25 min. is required. W. H. C. Shaw

3928. **Rapid method for the detection of quaternary ammonium salts in milk and wine. II.** J. Bastianutti (Lab. Chim. Prov., Udine, Italy). *Boll. Lab. Chim. Provinciali*, 1960, **11** (4), 732–737.—Suitable procedures are described for the extraction of quaternary ammonium compounds from milk and wine for subsequent identification by paper chromatography (*cf. Anal. Abstr.*, 1961, **8**, 3792). Milk samples are coagulated with rennet, filtered, and extracted with butanol. Wine samples are extracted with ether and then with butanol. The residue from the butanol extract of wine is decolorised by treatment with H_2O_2 and aq. NH_3 and re-extracted with butanol. The final butanol extracts are evaporated to small bulk for chromatography. By this method 5 mg of quaternary ammonium salt per litre of milk or wine can be detected. E. C. Apling

3929. **Analysis for citric acid in presence of casein.** J. R. Marier and M. Boulet ((Nat. Res. Council, Ottawa, Canada). *J. Dairy Sci.*, 1960, **43** (10), 1414–1420.—Errors due to turbidity and to adsorption of citric acid on casein pptd. at its isoelectric point or with trichloroacetic acid in the pyridine - acetic anhydride method described previously (*cf. Anal. Abstr.*, 1959, **6**, 3762) are eliminated by adjusting the pH of the sample aliquot to >12·3. Satisfactory results are obtained on skim-milk and casein solutions. W. H. C. Shaw

3930. **Sunset Yellow FCF for use in foodstuffs.** British Standards Institution (2 Park Street, London, W.1). B.S. 3340:1961. 6 pp.—Tests for purity and total dye content are given for Sunset Yellow FCF (C.I. Food Yellow 3).

3931. **Amaranth for use in foodstuffs.** British Standards Institution (2 Park Street, London, W.1). B.S. 3341:1961. 6 pp.—Tests for purity and total dye content are given for amaranth (C.I. Food Red 9).

3932. **Ponceau 4R for use in foodstuffs.** British Standards Institution (2 Park Street, London, W.1). B.S. 3342:1961. 6 pp.—Tests for purity and total dye content are given for Ponceau 4R (C.I. Food Red 7).

3933. **Carmoisine for use in foodstuffs.** British Standards Institution (2 Park Street, London, W.1). B.S. 3343:1961. 6 pp.—Tests for purity and total dye content are given for Carmoisine (C.I. Food Red 3).

3934. **Use of benzidine acetate for the detection of adulteration in animal feeding-stuffs and for the nephelometric detection of formaldehyde in milk.** G. Valentinis (Lab. Chim. Prov., Udine, Italy). *Boll. Lab. Chim. Provinciali*, 1960, **11** (4), 703–709.—Two novel uses of benzidine acetate (20% in glacial acetic acid) are described. For the detection of various adulterants in feeding-stuffs, the sample is spread on a white tile, wetted with glacial acetic acid and spotted with benzidine reagent. A brick-red colour develops on pieces of sawdust, peanut shells, rice hulls, cereal chaff, etc., which are readily detected when present in an amount $> \simeq 2\%$. For the detection of formaldehyde in milk, acidify the milk sample (100 ml) with 2N-H_2SO_4 (10 ml) and

distil 25 ml. Mix the distillate (5 ml) with reagent (1·5 ml). In the absence of formaldehyde the mixture remains clear indefinitely, but amounts of formaldehyde > 38 μg per ml of milk are detected by the slow (or rapid) production of a turbidity.

E. C. APLING

3935. **Chromatographic detection of sorbic acid in wine.** B. Romani and J. Bastianutti (Lab. Chim. Prov., Udine, Italy). *Boll. Lab. Chim. Provinciali*, 1960, **11** (4), 686–692.—Sorbic acid is separated from wine by steam-distillation after removal of alcohol by distillation in alkaline medium and subsequent acidification. The steam-distillate is extracted with ethyl ether and the extract is submitted to chromatography on Whatman No. 1 paper, with a mixture of n-butanol, 25% aq. NH_3 and water (7:2:1) as mobile phase. Sorbic acid is detected by its blue-green fluorescence under u.v. light when the chromatogram is treated with quinine soln. (R_F = 0·93). By this method, 10 mg of sorbic acid per litre of wine can be detected. E. C. APLING

3936. **Determination of polyoxyethylene glycols in bread.** D. Coppini and G. Bertolani (Lab. Chim. Prov., Modena, Italy). *Boll. Lab. Chim. Provinciali*, 1960, **11** (4), 697–702.—The method is based on the iodimetric method for Carbowax of Coppini and Grassi (*Atti Soc. Nat. Mat., Modena*, 1954, **85**, 1) after extraction of the sample with $CHCl_3$ and saponification of the extract. *Procedure*—Extract the dry sample (30 g) with $CHCl_3$ in a Soxhlet apparatus for 5 hr., evaporate the extract to dryness, saponify with 40% NaOH soln. (10 ml) and again evaporate to dryness. Boil the residue for 30 min. with $CHCl_3$ (50 ml), cool, filter and wash the filter with $CHCl_3$ (10 ml). Evaporate the combined extracts and dissolve the residue in water (5 ml). Add 0·1N-iodine (20 ml) and allow the brown ppt. formed to settle for 1 hr. Centrifuge for 15 to 20 min., decant the supernatant liquid and wash the ppt. with water (3 × 5 ml). To the ppt. add 10% KI soln. (5 ml) and $CHCl_3$ (5 ml). Shake mechanically and titrate with 0·1N-$Na_2S_2O_3$, with starch as indicator (1 ml ≡ 4·521 mg of Carbowax). Recoveries of Carbowax added to bread varied from 98 to 100%. E. C. APLING

3937. **Photometric determination of biphenyl and o-hydroxybiphenyl in citrus-fruit peel.** H. Böhme and G. Hofmann (Inst. f. Pharm.- u. Lebensmittelchem., Univ., Marburg/Lahn, Germany). *Z. LebensmittUntersuch.*, 1961, **114** (2), 97–105.—To determine biphenyl (**I**), the sample (from 100 g of fruit) is comminuted with water, 2 ml of cyclohexane is added and the mixture is distilled in the apparatus of Böhme and Bertling (*Ibid.*, 1957, **105**, 311). The mixture of volatile oils and **I** is dissolved in light petroleum and passed through a column of acid alumina (Woelm); the **I**, which alone is quant. retained, is eluted with $CHCl_3$, and nitrated in $CHCl_3$ soln. with HNO_3 (98·6%). The nitro-compounds obtained after evaporation of the washed $CHCl_3$ soln. are reduced to amino-compounds, which are then diazotised and coupled with *N*-1-naphthylethylenediamine hydrochloride to form a dye which can be determined by photometric measurement at 560 mμ. For the detection of *o*-hydroxybiphenyl (**II**), a portion of the light petroleum soln. is shaken with a borate buffer (pH 9·3) and methanol, and a soln. of 2,6-dibromo-*p*-benzoquinone-4-chlorimine in methanol is added; a blue coloration indicates the presence of **II**. For its determination, a sample of 300 to 400 g of fruit is needed, and the comminuted mixture must be steam-distilled with the addition of H_3PO_4 to obtain the whole of the **II** with the volatile oils. The **II** is eluted from the alumina column by continuous extraction with isopropyl alcohol. The colorimetric determination depends on the formation of a dye (with max. absorption at 480 mμ) by coupling **II** with Fast blue salt B (C.I. Azoic Diazo Component 48). Calibration graphs (linear up to 4 mg) are given for **I** and **II**. P. S. ARUP

3938. **Complexometric determination of antioxidants. V. Semi-micro determination of ethyl gallate in lard.** B. A. J. Sedláček (Inst. f. Ernährungsforsch., Prague, Czechoslovakia). *Z. LebensmittUntersuch.*, 1961, **114** (2), 127–128.—The method previously described for propyl gallate (*Anal. Abstr.*, 1960, **7**, 4014) is modified by prolonging the time of boiling the ethyl gallate soln. with the mercuric acetate soln. to 15 min., and by the use of 0·002M-EDTA and 0·002M-$ZnSO_4$ in the titrations. Recoveries of ethyl gallate from lard are close to the theoretical values. P. S. ARUP

3939. **Spectrophotometric measurements of theaflavines and thearubigins in black-tea liquors in assessments of quality in teas.** E. A. H. Roberts and R. F. Smith (Indian Tea Ass., Butler's Wharf, London). *Analyst*, 1961, **86**, 94–98.—A 50-ml aliquot of an infusion of tea (9 g) in 375 ml of water is extracted with isobutyl methyl ketone (50 ml). A 4-ml portion of the organic layer is diluted to 25 ml with methanol (soln. *A*) and 2 ml of the aq. layer to 10 ml with water and then to 25 ml with methanol (soln. *B*). A 25-ml portion of the original organic layer is shaken with 2·5% $NaHCO_3$ soln., and 4 ml of this washed organic phase is diluted to 25 ml with methanol (soln. *C*). To 2 ml of the aq. layer from the first extraction are added 6 ml of water, 2 ml of satd. oxalic acid soln. and then methanol to 25 ml (soln. *D*). The extinctions of each soln. (E_A, E_B, E_C and E_D) are measured at 380 mμ and at 460 mμ. The extinctions E_C at 380 mμ and 460 mμ are multiplied by 2·25 and 6·69, respectively, to give the theaflavine gallate content (%). The thearubigin content is 7·06 × ($2E_D + E_A - E_C$), the extinctions being measured at 380 mμ. If these extinctions are measured also at 460 mμ, the ratio of E_{380} to E_{460} (ranging from 3·6 to 8·2) (where $E = 2E_D + E_A - E_C$) indicates the colour of the thearubigins at 460 mμ, high ratios indicating a pale and low ratios a deeper colour. Although the thearubigin content is always greater than the theaflavine content, the more intensely coloured theaflavines contribute significantly to the colours preferred by tasters.

A. O. JONES

3940. **Determination of furfuryl alcohol in fruit juices and concentrates.** P. Dupaigne. *Ann. Falsif.*, 1961, **54**, 21–28.—U.v. spectrophotometry, paper chromatography, polarography, extraction, and colorimetry are all considered adequate for determining the larger quantities of furfuryl alcohol found, but only two modified colorimetric methods were satisfactory for traces (0·25 to 2·5 mg per litre). (*i*) Winkler's method (*Z. LebensmittUntersuch.*, 1955, **102**, 161) modified by replacing the malonylurea with HCl, carrying out the reaction at 0°, and using a stronger reagent, gives colours stable for 20 to 30 min. The reagent does not keep for more than a few hours. (*ii*) The A.O.A.C. method ("Methods of Analysis", 8th Ed., 1955, p. 141), modified by replacing acetic acid with HCl and carrying out

the reaction at 0°, gives colours stable for at least 1 hr. In either method, cloudy juices must be clarified by filtration or centrifuging, and coloured juices must be decolorised by, *e.g.*, mercuric acetate or activated charcoal. R. CLARKE

3941. **A co-precipitation and spectrophotometric determination of micro quantities of iron in Japanese brewing water and liquor.** Kiyoteru Otozai and Kunihiko Mizumoto (Dept. of Chem., Fac. Sci., Osaka Univ., Japan). *Mikrochim. Acta*, 1961, (2), 217–226 (in English).—A concentration technique is described that enables Fe to be determined in aq. soln. with a sensitivity of 0·0002 p.p.m. *Procedure*—To the sample soln. (500 ml), containing >40 μg of Fe, add 6N-HCl (2 ml) and 1% $KMnO_4$ soln. (2 ml) and boil. Make alkaline with 6N-aq. NH_3 and add 10% hydroxyammonium chloride soln. until the red colour of permanganate is discharged. Set aside for several hours. Collect the pptd. MnO_2 by decantation and centrifuging, wash with dil. aq. NH_3, dissolve in 6N-HCl (1 ml) and 10% hydroxyammonium chloride soln. (1 ml) and dilute to 10 ml. Add 2M-Na acetate (4·0 ml) and 0·25% 1,10-phenanthroline soln. (1 ml) and dilute to 20 ml. Set aside for 1 hr. at room temp., then measure the extinction at 510 mμ. Up to 100 p.p.m. of P added as pyrophosphate is without effect. The precision of the method is 0·0002 p.p.m. of Fe for water samples and 0·005 p.p.m. of Fe for saké samples, which must be wet-ashed before collection of the Fe. W. T. CARTER

3942. **Spectrophotometric determination of benzoic acid in wine.** P. Jaulmes, R. Mestres and B. Mandrou (Fac. de Pharm., Univ. Montpellier, France). *Ann. Falsif.*, 1961, **54**, 84–95.—The peak-emergence method for determination of benzoic acid (Stanley, *J. Ass. Off. Agric. Chem.*, 1960, **43**, 587) has been applied to ether extracts of wine. White wine (20 ml) is extracted twice with 25 ml of ether. The extract is then treated twice with 5 ml of N-NaOH plus 5 ml of water. The aq. layer is evaporated on a water bath to remove ether and, after cooling, treated with a mixture of 20 ml of aq. H_2SO_4 (2:3) and 20 ml of $K_2Cr_2O_7$ soln. (3·3 to 3·4%) for 1 hr. The soln., which should contain excess of $K_2Cr_2O_7$, is extracted twice with ether, the ether extract is washed with water and filtered, and the filtrate is made up to 50 ml with ether. The extract is then examined spectrophotometrically at 260 to 290 mμ. The peak-emergence is calculated and compared with a calibration curve. The method gives satisfactory results for concn. of benzoic acid $>$ 4 mg per litre of wine. The presence of small amounts of hydroxy- and chloro-benzoic acids does not cause significant error. S. M. MARSH

3943. **Detection of red hybrid characters in [grape] juice and wine.** G. Reuther (Inst. f. Züchtungsforschung, Bayer. Landesanst. f. Wein., Obst. u. Gartenbau, Würzburg, Germany). *Z. Lebensmitt-Untersuch.*, 1960, **113** (6), 480–484.—Previous work is discussed. In the method described, the colouring matters of grapes and grape-skins were extracted by maceration with N-HCl and examined by two-dimensional chromatography with n-butanol - glacial acetic acid - water (4:1:5). The substances were further identified by hydrolysis of the anthocyanins and chromatographic separation of the aglycones with n-butanol - 2N-HCl (1:1) and water - glacial acetic acid - HCl (10:30:3). In addition to the usual spray reagent (methanolic $AlCl_3$), spraying with Benedict's reagent was necessary to detect all the anthocyanins from wild vines. Extraction with n-butanol removes the interfering brown breakdown product in old red wines and also concentrates the anthocyanins. The diglycosides of the anthocyanidins of wild vines in red hybrid wines are more stable than the monoglycosides of red wines from *Vitis vinifera*. The detection of malvin is not alone sufficient for the accurate characterisation of a hybrid or adulterated wine. S.C.I. ABSTR.

3944. **Determination of succinic acid in sweet wine by means of ion exchangers.** V. Dimotaki-Kourakou (Inst. du Vin, Athens, Greece). *Ann. Falsif.*, 1961, **54**, 70–83.—Previous methods for the determination of succinic acid in wine are reviewed. It is shown that the method of Marignan (Thesis Doct. Pharm., Montpellier, 1944) is satisfactory for dry wines, and that wine does not contain any compounds that yield succinic acid on oxidation. The only constituent likely to produce such errors is glutamic acid, which is normally present in only negligible amounts. A modification of the Marignan method is proposed in which the double extraction is eliminated by passing the sample through a column of anion-exchange resin (Dowex 2, or Amberlite IRA-400) (carbonate form). Succinic acid is then eluted from the column with 10% ammonium carbonate soln. and the eluate is oxidised with $KMnO_4$ as in the original method. Satisfactory results are obtained for both sweet and dry wines. If the wine is rich in glutamic acid, this can be removed by passing the sample through a column of cation-exchange resin (Dowex 50 or Amberlite IRA-400). Full experimental details are given and typical results are quoted. S. M. MARSH

3945. **Methanol in spirits.** A. Castille (Fac. de Farm., Univ. Louvain, Belgium). *An. Bromatologia*, 1960, **12** (4), 335–340.—The determination of methanol as an impurity in distilled spirits by gas chromatography is described. A Fractovap apparatus is used, with a 1-metre column packed with Celite supporting polyoxyethylene glycol as stationary phase and operated at 90° ± 0·1°. The mobile phase is H at a flow rate of 2 litres per hr. With sample volumes of 0·02 ml, the methanol content is evaluated from a standard graph relating peak areas to methanol concn. E. C. APLING

3946. **Proceedings of the fifth Italian Congress on the Study of Fatty Substances. II. Marketing, technology, analysis and biology.** Held at Bari, Oct. 13–16, 1960. *Riv. Ital. Sostanze Grasse*, 1961, **38** (2), 105–162.—The following papers of analytical interest are included, all in Italian. **Classical and modern methods of analysis of oils and fats,** H. A. Bockenoogen, 105–111. **Gas-chromatographic studies on olive oil, and the possibility of controlling its genuineness,** M. Vitagliano, A. M. Leone and A. Vodret, 111–120. **The influence of technique on the amount of iron in expressed olive oil [determination of iron],** B. Foresti, 121–124. **Measurement of the colour of [olive] oils by the trichromatic method,** G. Fiorenzi, 125–127. **Quantitative vapour-phase chromatography of the methyl esters of fatty acids. II,** F. De Francesco and D. Avancini, 128–131. **Application of [ultra-violet] spectrophotometry to the analysis of olive oil. III. Identification of virgin olive oil,** A. Montefredine, L. Laporta and M. Jacone, 131–135. **Detection of foreign animal and**

vegetable oils in olive oil, B. Doro and V. Sadini, 135–140. **Methanolysis and ethanolysis in relation to the adulteration of olive oil,** L. Lipparini, 142–143.

3947. **Paper chromatography in the field of fats. XLIV. Analysis of glycerides.** H. P. Kaufmann and Z. Makus (Dtsch. Inst. für Fettforsch., Münster, Germany). *Fette, Seif., Anstrichmitt.*, 1961, **63** (2), 125–132.—The stationary phase is filter-paper impregnated with undecane, and the mobile phase acetic acid or acetone - methyl cyanide. The spots are located with Sudan black B (C.I. Solvent Black 3). The concept of a paper-chromatographic value ("p.c.v.") for each glyceride is developed; p.c.v. is proportional to the R_F value, and $= n - 2m$, where n and m are, respectively, the number of C atoms and the number of double bonds in the fatty acids. Glycerides having the same paper-chromatographic value cannot be separated by this method; if the values differ by 2 units, zone chromatography is necessary; for other cases, normal chromatography can be used. The analysis of mixtures of synthetic glycerides and natural glycerides is described, and the identification of the spots is carried out by saponification on the paper followed by two-dimensional chromatography of the acids, or by using standards of synthetic glycerides. R. CLARKE

3948. **Gas-chromatographic analysis of high-molecular-weight fat derivatives without the use of vacuum.** V. Vasilescu (Phys.-chem. Lab., VEB Dtsch. Hydrierwerk Rodleben, Germany). *Fette, Seif., Anstrichmitt.*, 1961, **63** (2), 132–138.—Modifications to an existing apparatus are described which include the heating of the absorption column to 280° to 300° and the vaporising zone to 350° to 400°, and the use of a conductivity cell which withstands 300°. The column packing is 20% Apiezon L oil on kieselguhr or certain polyesters on kaolin. The carrier gas is H at a rate of 50 to 100 ml per min. Typical chromatograms and conditions are given for synthetic fatty acids (C_8 to C_{22}) and natural fatty acids (C_{10} to C_{20}) in the form of their methyl esters; fatty alcohols (C_{10} to C_{22}), directly and in the form of their acetates; nitriles (C_{10} to C_{20}); natural and synthetic amines (C_{10} to C_{18}); and diphthalate esters of C_6 to C_{10} alcohols. Under specified conditions resolution of the following is also claimed—fatty acids and alcohols up to C_{26}; butyl esters of fatty acids; paraffins up to C_{32}; plasticisers, including dimethyl, dibutyl, dihexyl, diheptyl and di-(2-ethylhexyl) phthalates, sebacic acid diesters, and the triesters of hexanetriol and C_4 to C_8 fatty acids. R. CLARKE

3949. **Determination of fatty acids in lipids by gas chromatography. I.** F. De Francesco and D. Avancini (Staz. Sperimentale di S. Michele a/A, Trento, Italy). *Olii Min.*, 1960, **37** (11), 479–486.—Conditions for the separation of the methyl esters of the C_8 to C_{24} fatty acids by gas - liquid chromatography with an ethylene glycol succinate stationary phase, and a method for their quant. determination have been established. Results for the acids of 17 oils and fats are given. L. A. O'NEILL

3950. **Influence of column support on separation of fatty acid methyl esters by gas chromatography.** I. Hornstein and P. F. Crowe (Meat Lab., E. Utilization Res. and Devel. Div., U.S. Dept. Agric., Beltsville, Md.). *Anal. Chem.*, 1961, **33** (2), 310–311.—A comparison was made between Chromosorb R, Celite 545 and glass micro-beads as column support. The partitioning medium was 15% of poly(vinyl acetate) by wt. on the first two supports, and 0·25% of poly(vinyl acetate) by wt. on the beads. The helium flow rate was 83 ml per min., the column 9 ft. long, and a thermal-conductivity detector was used. Chromosorb and Celite gave uniformly good results with $\simeq$ 300-μg samples of fatty acid methyl esters, but the micro-beads, although giving rapid results at relatively low operating temp., gave peaks that were too poorly resolved to be of value. C. B. BAINES

3951. **Paper-chromatographic study and determination of iso-oleic acid during the hydrogenation of sunflower-seed oil. II. Use of iodine-131.** V. Koman and E. Komanová (Dept. Tech. Microbiol. and Biochem., Inst. Chem. Technol., Bratislava, Czechoslovakia). *Chem. Zvesti*, 1961, **15** (2), 136–142.—The chromatogram strips of the separated fatty acids (*Anal. Abstr.*, 1961, **8**, 2652) were immersed in 0·0022M-NaI and 0·044M-$NaIO_3$. A soln. of NaI in 0·025M-H_2SO_4 containing ^{131}I equiv. to 5 μC per ml was added, and after 150 min. the excess of ^{131}I was removed by drying the paper at room temp. for 12 hr., and the activity of the strips was measured. The results had an accuracy of $\pm$5·8%. J. ZÝKA

3952. **Microbiological methods for assaying panthenol.** N. Å. Diding and S. Weiland (Apotekens Kontrollab., Stockholm, Sweden). *Svensk Farm. Tidskr.*, 1960, **64** (32), 809–816 (in English).—The microbiological assay of panthenol by measuring its inhibitive effect on *Leuconostoc mesenteroides* (Bird and McCready, *Anal. Chem.*, 1958, **30**, 2045) was found to be satisfactory. The effects of modifying the assay medium and varying the size of inoculum and the incubation time were studied. With a modified medium consisting of Difco pantothenate medium plus 1% of photolysed peptone and 0·2% of Tween 40 (double strength medium) a more vigorous growth is obtained than with the medium originally described. P. PEDERSEN

3953. **Quantitative determination of ascorbic acid by paper chromatography.** M. Milletti (Univ. of Cagliari, Italy). *Ann. Chim., Roma*, 1960, **50** (12), 1685–1692.—For amounts of ascorbic acid of 1 to 100 μg, the areas of the spots obtained on a paper chromatogram (with a descending technique for >15 μg and a horizontal technique for <15 μg) are measured planimetrically after being revealed with ammoniacal $AgNO_3$ soln. For amounts >400 μg the eluted acid is titrated with 0·0002M-2,6-dichlorophenolindophenol. Within these ranges the error should be $\simeq$ 6%. For amounts of 100 to 400 μg, the titration method may be used, but the error will be rather higher. L. A. O'NEILL

3954. **Spectrophotometric measurements on ascorbic acid and their use for the estimation of ascorbic acid and dehydroascorbic acid in plant tissues.** E. J. Hewitt and G. J. Dickes (Res. Sta., Long Ashton, Bristol, England). *Biochem. J.*, 1961, **78** (2), 384–391.—The u.v. spectrophotometric method described can be applied to as little as 10 mg of plant tissue. From 1 to 75 μg of either acid can be determined in 3 ml of extract, with an accuracy within 5% for 2 μg and 2% for 10 to 20 μg. The tissues are extracted with 2% Cu-free HPO_3 soln. and the extinction is measured at 265 mμ. A second portion of the extract is treated with homocysteine or H_2S to reduce the dehydroascorbic acid to ascorbic acid and the extinction is measured again. A third portion is treated with ascorbic

acid oxidase, and the extinction is again measured. The amounts of both acids can be calculated from these results. The method is more specific than those based on the use of indophenol and is at least as sensitive and as easy to apply.

J. N. ASHLEY

3955. **Analysis of tocopherol mixtures by thin-layer chromatography.** A. Seher (Dtsch. Inst. für Fettforsch., Münster i. W., Germany). *Mikrochim. Acta*, 1961, (2), 308–313 (in German).—Tocopherol mixtures are separated by this technique on silica gel with $CHCl_3$ as solvent or on alumina with benzene as solvent. The separated compounds are located by spraying the chromatogram with a 20% soln. of molybdophosphoric acid in ethanol, and then exposure to gaseous NH_3. The tocopherols give blue spots on a white background. The β- and γ-tocopherols are not completely separated, but can be differentiated with ceric sulphate, which gives a brown colour with β-tocopherol and a blue colour with γ-tocopherol. The results can be made semi-quantitative by measuring the area of the spots.

W. T. CARTER

See also Abstracts—**3561**: *Section VI*, Fruit esters in spirits. **3783**, Paper-chromatographic detection of fatty aldehydes, ketones and keto-acids. **3806**, Determination of vanillin. **3828**, **3829**, Detection of food dyes. **3881**, Cholesterol and squalene in oils.

Sanitation

Analysis of air, water, sewage, industrial wastes, industrial poisons.

3956. **The pyridine - alkali reaction as a basis for the determination of chlorinated aliphatic hydrocarbons.** G. A. Hunold and B. Schühlein (Inst. f. Wasser, Boden u. Lufthygiene, Lab. für Chem. Toxikol., Berlin). *Z. anal. Chem.*, 1961, **179** (2), 81–91 (in German).—The several published variants of the Fujiwara reaction are reviewed and optimum conditions are given for the determination of $CHCl_3$, CCl_4, dichloro- and tetrachloro-ethane, trichloro- and tetrachloro-ethylene, and 2-chloroethanol in the atmosphere.

T. R. ANDREW

3957. **Simplified test for sexavalent chromium.** B. L. Goodman (Sewage Treatment Plant, Warren, Mich., U.S.A.). *Wat. & Sewage Wks*, 1961, **108** (2), 80.—The American standard method ("Standard Methods for the Examination of Water, Sewage and Industrial Wastes," 10th Ed., APHA, AWWA & WPCF, New York, 1955) is modified by the use of a single reagent in powder form, prepared by grinding together 1,5-diphenylcarbazide (0·25 g) and tartaric acid (9·75 g). *Procedure*—To the sample, or a suitable dilution (containing ≃1 p.p.m. of Cr^{VI}), add the reagent powder (0·1 g), stir to dissolve, set aside for 5 min., and measure the extinction at 540 mμ. Alternative permanent colour standards, prepared from dilutions of the crystal violet and safranine stains used in the Gram technique, are described. The reagent and colour standards are permanently stable and the results are identical with those of the standard method.

E. C. APLING

3958. **Spectrochemical determination of boron in saline waters.** R. C. Reynolds, jun., and J. Wilson (Pan American Petroleum Corp., Tulsa, Okla., U.S.A.). *Anal. Chem.*, 1961, **33** (2), 247–249.—From 0·4 to 8 p.p.m. of boron in sea-water (10 ml) can be determined to within ≃±3% by high-voltage spark excitation of the sample by the rotating-disc method (Harvey, "Spectrochemical Procedures," Appl. Res. Lab., Glendale, Calif., 1950, pp. 323, 346), with Be as internal standard. The intensity ratio of B 2498 A to Be 2494 A is obtained and is referred to a working curve.

W. J. BAKER

3959. **Determination of microgram amounts of amino-acids in natural water.** A. D. Semenov, I. N. Ivleva and V. G. Datsko (Hydro. Chem. Inst., Acad. Sci., USSR). *Izv. Akad. Nauk SSSR*, 1961, (1), 184–186.—The method is based on the reaction of an amino-acid with ninhydrin to give a blue-violet colour, which is stabilised by the addition of Cd^{2+}. *Procedure*—Pass 1 litre of the water violet colour, which is stabilised by the addition of Cd^{2+}. *Procedure*—Pass 1 litre of the water through a column (1 cm × 20 cm) of cation exchanger KU-2 or KU-6 (H^+ form) at a rate of 10 to 12 drops per min. Elute the amino-acid with 2N-aq. NH_3 (80 ml) and evaporate the eluate to dryness in a porcelain dish. Wash the dried residue into a 50-ml flask with 2 ml of H_2O and add 1 ml of ninhydrin reagent (75 mg of $CdCl_2$, 6 ml of H_2O, 0·3 ml of glacial acetic acid and 2 g of ninhydrin in 100 ml of acetone), 2 drops of satd. $CdCl_2$ soln. and 5 ml of butanol. Stopper the flask and heat for 15 min. in boiling water; after cooling, transfer the mixture to a calibrated test-tube with 25% K Na tartrate soln. (1 ml), make the alcohol layer up to 6 ml and centrifuge. To 5 ml of the alcohol layer add 0·3 ml of butanol to destroy the emulsion and measure the extinction at 505 mμ. Obtain a calibration curve by taking known amounts of glycine through the procedure. As little as 1 μg of N can be determined.

J. W. PRICE

See also Abstracts—**3561**: *Section Va*, Cu, Pb and Cd in water. **3712**, Indicator for Cl^-. **3916**, Detection of warfarin. **3941**, Fe in water.

Agricultural analysis

Soil, fertilisers, herbicides, pesticides, animal feeding-stuffs.

3960. **Analysis of carotenoids in maize grain.** F. W. Quackenbush, G. Firch, W. J. Rabourn, M. McQuistan, E. N. Petzold and T. E. Kargl (Dept. Biochem., Purdue Univ., Lafayette, Ind., U.S.A.). *J. Agric. Food Chem.*, 1961, **9** (2), 132–135.—The ground maize (100 g) is quant. extracted by a mixture of hexane (15%), acetone (75%) and water (10%), and the org. phase is separated for chromatographic analysis on a column of MgO (covered by a 1-cm layer of anhyd. $MgSO_4$). The polyene fraction containing the β-carotene, β-zeacarotene and ζ-carotene (together with phytoene and phytofluene) is eluted by hexane (5 ml) followed by hexane containing 5% of acetone (100 ml). The amounts and relative proportions of the three provitamins A are determined by spectrophotometric measurements at different wavelengths (tabulated) and compared with data for mixtures of known composition. The necessary working details are tabulated for the elution and spectrophotometric analysis of six further carotenoid fractions. The reproducibility of the method is satisfactory. Provitamin activities calculated from

the results agree well with the results of bioassay tests with rats. P. S. ARUP

3961. Routine analysis of carbohydrates and lignin in herbage. R. E. Deriaz (Grassland Res. Inst., Hurley, Berks., England). *J. Sci. Food Agric.*, 1961, **12** (2), 152–160.—A rapid procedure is described for the fractionation of herbage material into (*i*) soluble carbohydrate, (*ii*) structural pentosans, (*iii*) structural hexosans and (*iv*) crude lignin. The dried, milled sample is freed from fats, waxes and pigments by extraction with ethyl ether for 72 hr. in a Soxhlet apparatus. The residue is then extracted with 0·5% ammonium oxalate soln. by heating under reflux for 2 hr. The insoluble residue is separated and washed by centrifugation and decantation and submitted to successive extractions with N-H_2SO_4 and 72% H_2SO_4. The final residue is dried, weighed and ignited to determine lignin, and the residue obtained by similar treatment of a second sample is analysed for nitrogen by the Kjeldahl method to give a correction for protein. Soluble carbohydrates are determined on the ammonium oxalate extract by anthrone colorimetry by the method of Fairbairn (*Chem. & Ind.*, 1953, 86) (slightly modified), and the combined acid extracts are analysed for pentosans with aniline - acetic acid - oxalic acid soln. (Tracey, *Biochem. J.*, 1950, **47**, 433) and for hexosans with chromotropic acid (Klein and Weissman, *Brit. Abstr. C*, 1953, 474). The agreement between duplicates for each carbohydrate fraction was within ±4% of the mean. J. R. HUDSON

3962. Determination of total potassium in soil by using the spirit flame-photometer. P. G. Grabarov and E. A. Solodnikova. *Izv. Akad. Nauk KazSSR, Ser. Botan. i Pochvoved.*, 1959 (1960), [**3** (6)], 44–47; *Ref. Zhur., Khim.*, 1960, (20), Abstr. No. 80,750.—The flame photometer with a spirit burner is used (*Ref. Zhur., Khim.*, 1960, Abstr. No. 26,219). Sinter 0·5 g of sample for 3 hr. at 800° with 0·5 g of NH_4Cl and 2 g of $CaCO_3$, extract with water, filter the soln. and make up to 500 ml. To remove Ca, heat 200 ml of the soln. almost to boiling, add 25 ml of 10% ammonium carbonate soln., heat for 20 min. at 85° to 90°, dilute to 250 ml and measure the extinction of the soln. after allowing the ppt. to settle or after filtering. The results of determining K (1·3 to 3·5% of K_2O) in soil obtained by this method agree well with those of the cobaltinitrite method and the flame-photometric method with the acetylene - air flame. C. D. KOPKIN

3963. Determination of total phosphorus in soil. M. N. Burangulova and G. F. Galimov. *Izv. Sibirsk. Otd., Akad. Nauk SSSR*, 1960, (2), 97–103; *Ref. Zhur., Khim.*, 1960, (22), Abstr. No. 88,320.—The following reducing agent is proposed for the determination of P in soil—$NaHSO_3$ (21·922 g), Na_2SO_3 (0·8 g) and 1-amino-2-naphthol-4-sulphonic acid (0·25 g) per 100 ml of H_2O. Heat the soil sample (0·5 to 1·0 g) in a Kjeldahl flask with conc. H_2SO_4 (5 to 12 ml) for 20 to 25 min., add $KClO_4$ (100 to 200 mg) and heat the soln. until it is colourless (15 to 20 min.); cool, add H_2O (150 ml) and filter. Neutralise a 20-ml aliquot of the filtrate to 2,6-dinitrophenol with 10% aq. NH_3, add N-H_2SO_4 (1 drop), dilute, heat to 40°, add 2·5% $(NH_4)_2MoO_4$ soln. (5 ml) and the reducing agent (2 ml). Cool the soln., dilute it to 50 ml and measure the colour with a red filter. The colour is stable for 30 min.; the error is 3·3%. K. R. COOK

3964. Differential thermal analysis of humic substances and related materials. B. D. Mitchell. *Sci. Proc. Roy. Dublin Soc., Ser. A*, 1960, **1** (4), 105–114.—The complete combustion curves have been recorded of peat and its principal components—holocellulose, lignin and "humic acid." It has been shown that the curve for peat is related to its botanical origin and degree of humification, and that the area under the exothermic peaks of this curve gives a measure of the calorific value of the peat. It is considered that the major exothermic peaks may serve to differentiate between the carbohydrate component and the complex aromatic materials present. FUEL ABSTR. AND CURR. TITLES

3965. Spectrographic determination of boron and manganese in superphosphate. J. Hřivnáček (Res. Inst. Agrochem. Technol., Bratislava-Predmestie, Czechoslovakia). *Sb. Prác. Výzk. Úst. Agrochem. Technol., Bratislava*, 1961, **1**, 113–116.—*Procedure*—Dissolve the sample (0·5 g) in HCl (5%) (50 ml), and dilute with H_2O to 100 ml. Transfer 5 to 25 ml to a 50-ml flask, add $SnCl_2$ soln. (10%) (2·5 ml) as internal standard and DBN-12 (polyoxyethylated dibenzyl-2-naphthol) soln. (10%) (1 ml) as emulsifier and dilute with HCl (2·5%) to vol. Carry out the spectrographic analysis in a Hilger E-492 spectrograph, with a rotating electrode (SU-401) and the lines B 2497·733 A and Mn 2576·10 A. Calibration curves were prepared with standard soln. containing 0·01, 0·1 and 1·0 mg of B or Mn per ml. J. ZÝKA

3966. Quantitative determination of coumestrol in fresh and dried lucerne. A. L. Livingston, E. M. Bickhoff, J. Guggolz and C. R. Thompson (West. Reg. Res. Lab., Agric. Res. Service, U.S. Dept. of Agric., Albany, Calif., U.S.A.). *J. Agric. Food Chem.*, 1961, **9** (2), 135–137.—The method described is suitable for routine tests; it is sensitive to 2 p.p.m. of coumestrol and accurate to within ±5%. Filtered 95% ethanolic extracts of the fresh material (400 g) (obtained by high-speed blending) or of the powdered dry material (20 g) (obtained by rehydration and steeping in ethanol for 24 hr.) are extracted with light petroleum (4 × 35 ml); the aq. ethanolic phase is evaporated under reduced pressure to 20 to 25 ml, the conc. soln. is extracted with ethyl ether (15 ml, 4 × 8 ml) and further concentrated for paper-chromatographic analysis by the method previously described (Livingston *et al.*, *Anal. Abstr.*, 1961, **8**, 2569) with the instrument described by Bailey (*Anal. Chem.*, 1960, **32**, 1726) to measure the fluorescence of the coumestrol spots; an ascending solvent containing acetic acid, water and HCl (10:7:3) is substituted for that previously used. Fluorescence values are evaluated by comparison with results obtained from known amounts of coumestrol. P. S. ARUP

3967. Colorimetric determination of nihydrazone (HC-064) in feeds. L. R. Stone (Hess & Clark, Ashland, Ohio, U.S.A.). *J. Ass. Off. Agric. Chem.*, 1961, **44** (1), 2–4.—The nihydrazone (5-nitro-2-furaldehyde acetylhydrazone) is extracted with 95% aq. dimethylformamide at 90°; the soln. is passed through a column containing Al_2O_3 and $Mg(OH)_2$, and aliquots are treated with acidified phenylhydrazine hydrochloride soln. (*a*) directly, and (*b*) after reduction with $Na_2S_2O_4$. The samples are kept at 40° for 20 min., cooled to 15°, and shaken with toluene, the extinction of the toluene layer being read at 440 mμ and compared with standards.

Collaborative average results were within 10% of the true values (0·007, 0·012%).

A. A. ELDRIDGE

3968. **Improved method for determination of Zoalene [3,5-dinitro-o-toluamide] in feeds.** M. E. Getzendaner and W. L. Garner (Dow Chemical Co., Midland, Mich., U.S.A.). *J. Ass. Off. Agric. Chem.*, 1961, **44** (1), 18–26.—A study of the method previously described (Getzendaner, *Ibid.*, 1960, **43**, 287), with collaborative results, is presented. The extractant recommended is 85% aq. methyl cyanide. Since colour fading occurs above 30°, any considerable rise in temperature on addition of ethylenediamine is avoided by first evaporating an aliquot of the extract to dryness and re-dissolving the residue in 95% dimethylformamide. Blanks are reduced by treating the extract with Al_2O_3.

A. A. ELDRIDGE

3969. **Assay for Enheptin A [2-acetamido-5-nitrothiazole] in finished feeds.** M. H. Woolford, jun. (Agric. Div., American Cyanamid Co., Princeton, N.J., U.S.A.). *J. Ass. Off. Agric. Chem.*, 1961, **44** (1), 26–29.—Senn's method (*Ibid.*, 1958, **41**, 329) for this determination has been modified by washing the alumina used for chromatography first with HCl and then with water. Satisfactory collaborative results are tabulated.

A. A. ELDRIDGE

3970. **Determination of nitrofurazone in feeds.** E. Puglisi (Eastern States Farmers' Exchange, Huron, Ohio, U.S.A.). *J. Ass. Off. Agric. Chem.*, 1961, **44** (1), 30–31.—A further modification of Stone's method (Merwin, *Ibid.*, 1960, **43**, 281) involves an increase in the amount of $Na_2S_2O_4$ used. Satisfactory collaborative results are tabulated.

A. A. ELDRIDGE

3971. **Determination of amprolium in feeds.** C. R. Szalkowski and E. P. Schulz (Merck and Co. Inc., Rahway, N.J., U.S.A.). *J. Ass. Off. Agric. Chem.*, 1961, **44** (1), 5–12.—The coccidiostat amprolium [1-(4-amino-2-n-propyl-5-pyrimidinylmethyl)-2-picolinium chloride], used at a concn. of 0·01 to 0·025%, is extracted by shaking with 67% aq. methanol, the extract being purified by passage through a column of Al_2O_3. Colour is developed in an aliquot of the percolate by means of a reagent comprising naphthalene-2,7-diol, $K_3Fe(CN)_6$, KCN and NaOH in aq. methanol. After centrifuging, the extinction of the clear liquid is read at 530 mμ. The extinctions of aq. methanol and of a standard soln. similarly treated are also determined. In collaborative tests the average recovery was 99·7% (range 83·2 to 112·8%).

A. A. ELDRIDGE

3972. **Revaluation of the fluorimetric method for the determination of Serpasil (reserpine) in feeds.** W. J. Mader, R. P. Haycock, P. B. Sheth, R. J. Connolly and P. M. Shapoe (Ciba Pharmaceutical Products Inc., Summit, N.J., U.S.A.). *J. Ass. Off. Agric. Chem.*, 1961, **44** (1), 13–17.—The method previously described (Mader *et al.*, *Ibid.*, 1960, **43**, 291) has been modified by reducing the number of extractions and omitting the evaporation step. The concn. of HNO_3 is a critical factor. Operational details are given and collaborative results reported.

A. A. ELDRIDGE

3973. **Microbiological method for assaying streptomycin in animal feeds.** J. J. Mayernik (Merck and Co., Inc., Rahway, N.J., U.S.A.). *J. Ass. Off. Agric. Chem.*, 1961, **44** (1), 33–42.—Kirshbaum's modification (with sulphadiazine) of Randall and Burton's method (*Ibid.*, 1957, **40**, 857) was applied to feeding-stuffs containing various amounts of streptomycin. The procedure is fully described. Concentrations (p.p.m.) and mean percentage recoveries for the four feeding-stuffs were, respectively—6176, 96·9; 27,638, 99·0; 18·7, 83·5; and 46·1, 89·1. Variance and confidence limits for the collaborative results are tabulated. The method appears to be capable of a precision of about ±23%.

A. A. ELDRIDGE

3974. **Analysis of mixtures of chlorinated 2-methylphenoxyacetic acids by ultra-violet spectrophotometry and paper chromatography.** V. Bátora, J. Kováč and E. Novomeská (Res. Inst. Agrochem. Technol., Bratislava-Predmestie, Czechoslovakia). *Sb. Prác. Výzk. Úst. Agrochem. Technol., Bratislava*, 1961, **1**, 33–39.—*Procedure*—The sample (≃15 to 300 μg) is chromatographed on S. & S. 2043 paper with isoamyl alcohol - aq. NH_3 - H_2O (6:3:1) as solvent. After 17 to 20 hr. the chromatograms are dried and heated at 125° to 130° to decompose the ammonium salts of the separated acids. The paper is moistened with a soln. of β-methylumbelliferone (0·025% in 33% ethanol, adjusted with aq. NH_3 to pH 8 to 9) and observed in u.v. light (dark spots on a slightly blue fluorescent background) (sensitivity, 3 μg). In a second sample the separated acids are extracted for 30 min. with methanol - 0·1N-HCl (17:3) (6 ml) and the extinctions are measured at 279 mμ and compared with standards; 4-chloro-2-methylphenoxyacetic acid can be determined in the presence of 6-chloro-2-methylphenoxyacetic acid.

J. ZÝKA

3975. **Chemical and biological examination of commercial pyrethrum extracts for insecticidal constituents.** R. M. Sawicki and E. M. Thain (Rothamsted Exp. Sta., Harpenden, Herts., England). *J. Sci. Food Agric.*, 1961, **12** (2), 137–145.—By extraction with nitromethane, typical commercial 25% pyrethrum extracts were shown to contain ≃22% of pyrethrins. Displacement chromatography on Al_2O_3 and elution with 0·75% myristic acid soln., followed by i.r. spectroscopy of the fractions, showed that the pyrethrins consisted of 42 to 47% of pyrethrin I, 13 to 25% of cinerin I, 20 to 31% of pyrethrin II, and 7·5 to 13·5% of cinerin II. The biological activities of the fractions were measured by toxicity tests on female house-flies; it was demonstrated that the activities decreased in the order pyrethrin II, pyrethrin I, cinerin I (and cinerin II). No other active constituents were detected.

J. R. HUDSON

3976. **Infra-red spectrophotometric analysis of technical hexachlorocyclohexane and mixtures of its isomers and heptachlorocyclohexane.** M. Livař (Res. Inst. Agrochem. Technol., Bratislava-Predmestie, Czechoslovakia). *Sb. Prác. Výzk. Úst. Agrochem. Technol., Bratislava*, 1961, **1**, 41–58.—A combination of the chromatographic method (Smrž, *Chem. Zvesti*, 1953, **7**, 197), with i.r. spectrophotometry yielded good results. Modifications of the methods are fully described.

J. ZÝKA

3977. **Determination of *OO*-dialkyl hydrogen phosphorodithioates and their sodium salts in technical products.** V. Bátora and Z. Veselá (Res. Inst. Agrochem. Technol., Bratislava-Predmestie, Czechoslovakia). *Sb. Prác. Výzk. Úst. Agrochem. Technol., Bratislava*, 1961, **1**, 85–89.—The sample is converted into the nickel salt, which is determined iodimetrically without preliminary isolation. Interference by H_2S or thiols is eliminated by the

formation of insol. NiS or mercaptide, respectively. *Procedure*—Add the sample (0·5 g) to a satd. soln. of $NiSO_4$ (3 ml); mix, add H_2O (40 ml) (the violet dimethyl nickel phosphorodithioate dissolves), then a known excess of 0·1N-iodine till the liquid becomes yellow, and back-titrate with 0·1N-$Na_2S_2O_3$, with starch as indicator. When determining *OO*-dialkyl sodium phosphorodithioate in the presence of the free acid, a preliminary neutralisation of the sample to methyl red must be carried out.

J. ZÝKA

See also Abstracts—**3560**: *Section IV*, Toxic phosphoric acid esters. **3561**: *Section VIIa*, I.r. spectrophotometry of pesticides. **3562**: *Section VIII*, Residues of pentachloronitrobenzene. Iodine in soil. **3606**, Mg in soil. **3608**, Cu and Mg in plants. **3916**, Detection of warfarin. **3934**, Detection of adulteration in feeding-stuffs.

5.—GENERAL TECHNIQUE AND APPARATUS

General

3978. **Automatic apparatus for treating liquids for analysis.** Technicon Instruments Corp. [Inventor: L. T. Skeggs]. Brit. Pat. 863,910; date appl. 17.11.58.—An automatic feeding device for supplying a series of samples in succession to the analysing apparatus comprises a rotatable circular plate driven by a motor and provided with recessed receptacles for holding the samples, which are agitated by a jet of air. An intake device is inserted successively into the receptacles and a metering pump and separate fluid passages are provided for concurrently pumping the sample and a processing liquid, in predetermined proportional amounts, to an analysing apparatus (*Anal. Abstr.*, 1957, **4**, 3803). The apparatus is mainly designed for the determination of glucose, urea, metal constituents, etc., in a series of samples of blood, urine and other body fluids.

J. M. JACOBS

3979. **Improvements relating to pipettes.** V. Morrill, jun. Brit. Pat. 866,529; date appl. 26.11.58.—The pipette comprises capillary-tube and aspirating-tube sections and an intermediate glass bulb the interior of which has a frosted surface. To facilitate mixing, the glass bulb is provided with an internal annular ridge, and may contain a glass bead.

J. M. JACOBS

3980. **Stop-action control of delivery from burettes.** M. A. Fill and E. H. Wren (Norwood Tech. Coll., London, S.E.27). *Lab. Practice*, 1961, **10** (2), 102–105.—Two simple modifications to the conventional type of burette-tap are described, with diagrams. A Bakelite chemical cap is sealed on to the burette key with sealing-wax. A wire stop is inserted in the wax so that when it contacts the delivery end of the burette a slow drop-rate is given, and when it contacts the burette tube above the stopcock barrel a full flow of liquid is given. A modification is described in which the stop consists of a bent glass rod sealed on to one arm of the stopcock key. The second stopcock described gives a very fine control and a rapid on - off action, and is suitable for micro-titrations and also for gases. Both types of tap are easy and convenient to use.

R. A. HENDEY

3981. **Application of the double-withdrawal countercurrent extraction technique to analytical chemistry.** J. O. Hibbits (General Electric Co., Cincinnati, Ohio, U.S.A.). *Anal. Chim. Acta*, 1961, **24** (2), 113–120 (in English).—A computer is applied to the mathematical treatment of the double-withdrawal countercurrent extraction technique. Theoretical recoveries for systems having 5 to 1001 stages are plotted in a series of graphs.

H. N. S.

3982. **Filtration losses during analytical extractions.** M. Marsh and G. Schill (Kungl. Farm. Inst., Stockholm, Sweden). *Svensk. Farm. Tidskr.*, 1960, **64** (36), 921–927.—Soln. of salicylic acid, amphetamine and procaine in $CHCl_3$ were filtered through filter-paper, cotton wool plus Na_2SO_4, glass wool and glass-fibre paper. Filter-paper gave the highest filtration losses and glass wool and glass-fibre paper the lowest.

P. PEDERSEN

3983. **Laboratory separating-funnels.** National Research Development Corp. [Inventor: I. E. Bush]. Brit. Pat. 865,246; date appl. 29.3.57.—A funnel for separating immiscible solvents comprises a tubular body with an inlet at its upper end, an outlet tube about half-way down the body and projecting at right angles to it, and a tap-controlled outlet at the lower end.

J. M. JACOBS

3984. **Semi-quantitative autoradiography with the ring-oven. I. General, apparatus and operation.** H. Weisz and L. J. Ottendorfer (Inst. für anal. Chem., Tech. Hochschule, Wien, Austria). *Mikrochim. Acta*, 1961, (2), 191–205 (in German).—Radioactive substances present in ring zones are determined by autoradiography by using an apparatus (described and illustrated) that allows 50 exposures of short sections of the ring to be taken automatically. The exposure time of each step is increased by a fixed percentage amount, and the resulting radiograph is a ring-shaped stepped grey wedge. This is compared with radiographs of rings prepared from standard soln. By rotating the unknown until it matches the standard it is possible to calculate the concn. of the unknown from the concn. of the standard and the exposure times. The methods of calculation are described in detail.

W. T. CARTER

3985. **New type of combustion flask for the micro-determination of nitrogen.** V. Fojtová and J. Purš (Fac. Transfus. Station, Prague). *Chem. Listy*, 1961, **55** (2), 201–203.—The flask is constructed by bending the neck of a test-tube (6 to 8 ml) at an angle of 135°; the loss of sample caused by spurting and dry combustion on the walls of the flask is thus prevented. The method was tested in the analysis of blood plasma and plant material. In all cases the statistical evaluation of the results showed a higher reliability of the suggested method as compared with the use of the conventional 50-ml Kjeldahl flask.

J. ZÝKA

3986. **Apparatus for simultaneously carrying out thermogravimetric, differential-thermal and derivative-thermogravimetric analysis.** F. Paulik, J. Paulik and L. Erdey. Brit. Pat. 865,073; date appl. 25.9.57.—The apparatus comprises a crucible for the test sample secured to one arm of a thermobalance beam, a stationary crucible for the inert comparison substance, two thermo-elements and a measuring instrument for derivative-thermogravimetric analysis connected with the other arm of the beam.

J. M. JACOBS

3987. **An improved viscometer.** Tyer & Co., Ltd. [Inventor: P. D. Saw]. Brit. Pat. 863,510;

date appl. 14.5.58.—The viscometer comprises a tube for the liquid to be tested and an oscillatory circuit, the frequency of which changes as a falling object (*e.g.*, a phosphor-bronze or copper-plated sphere to provide good high-frequency "skin" conductivity) in the tube passes two points spaced at a predetermined distance apart. Electronic means are provided whereby the changes of frequency are used for giving a visual indication of the time elapsing during the travel of the sphere between the two points. J. M. JACOBS

See also Abstract—**3561**: *Section VIIa*, Measurement of pH with indicators.

Chromatography, ion exchange, electrophoresis

3988. **Application of chelate systems to partition chromatography. Preliminary paper.** T. B. Pierce (A.E.R.E., Harwell, England). *Anal. Chim. Acta*, 1961, **24**, (2), 146–152 (in English).—Experiments are reported on the extraction behaviour of ^{64}Cu between aq. HCl and soln. of dithizone in $CHCl_3$ and CCl_4, respectively, retained on silica gel. The extraction *vs.* acidity curves are similar to corresponding curves for liquid - liquid extraction, and suggest the possibility of adapting the column principle for use in liquid - liquid extractions. The theory of such extractions is treated mathematically. H. N. S.

3989. **Chromatographic reagents for some organic substances.** R. A. Cadenas and J. O. Deferrari (Dept. Quím. Biol., Fac. de Cienc. Exact. y Nat., Buenos Aires, Argentina). *Analyst*, 1961, **86**, 132–134.—One chromatographic reagent (*A*) for certain nitrogenated compounds and two (*B* and *C*) for carbohydrates and their esters have been studied. Reagent *A* is 10% aq. $NaIO_4$ - 3·5% aq. picric acid (1:1). The chromatogram is sprayed with *A*, allowed to dry and heated at 110° for 5 to 15 min. A list of compounds giving a pink colour on a yellow background is given. Reagent *B* is a freshly made mixture of 2 vol. of 2% picric acid in methanol with 1 vol. of a 10% soln. of sodium in methanol. The procedure is as for reagent *A*. Reducing sugars and their acetyl or benzoyl esters give a pink colour on a yellow ground. Reagent *C* is a mixture of a 0·3% soln. of $AgNO_3$ in methanol, methanol saturated with NH_3, and a 7% soln. of sodium in methanol. The components are mixed just before use in the ratio 5:1:2, and the colour is developed by dipping the chromatogram in the mixture. Reducing and non-reducing carbohydrates and their acetic or benzoic esters produce brown or yellowish or greenish spots on a beige ground. A list of some of the compounds assayed with these reagents is given. A. O. JONES

3990. **Quantitative chromatographic methods. V. An improved ninhydrin - hydrindantin reagent.** A. T. Matheson, E. Tigane and C. S. Hanes (Dept. of Biochem., Univ. Toronto, Ontario, Canada). *Canad. J. Biochem. Physiol.*, 1961, **39** (2), 417–425.—A previous reagent (Connell *et al.*, *Ibid.*, 1955, **33**, 416) was found to be somewhat variable, owing to losses of hydrindantin by initial oxidation, and by deposition from the supersaturated soln. In the present modification, de-oxygenated solvents are used together with a satd. soln. of hydrindantin in equilibrium with the solid phase. *Preparation*—Ninhydrin (7·6 g) is dissolved in 1140 ml of redistilled 2-methoxyethanol; 610 ml of water and 250 ml of 4N-acetate buffer (pH 5·5) are added, and the soln. is de-aerated under vacuum for 15 min. then cooled to 5°. Then 1·2 g of hydrindantin is added, the mixture is shaken well, and stored under N at 5°. The reagent is designed for use by the addition of one-tenth of its vol. of water or aq. amino-acid soln. (saturated with air). It is stable for at least 9 months, and gives low and steady blank values. D. G. Moss

3991. **Quantitative trace analysis by X-ray fluorescence spectroscopy of paper chromatograms.** E. Jackwerth and H. G. Kloppenburg (Inst. f. Spektrochem. u. angew. Spektroskopie, Dortmund-Aplerbeck). *Z. anal. Chem.*, 1961, **179** (3), 186–196 (in German).—Paper chromatograms (10 mm wide) bearing various amounts of Zn, Ga and In were drawn behind an aperture (8 mm × 10 mm) inclined to the incident X-ray beam (Mo radiation, 40 kV, 40 mA) at an angle of 45°. The fluorescent radiation produced was passed through an analysing crystal of LiF, and the intensity for each element at the characteristic Bragg angle for its K line was determined with a scintillation tube. In the "impulse - R_F diagram" method the strips were drawn past the aperture at a speed of 2 mm per min. and the area under the resulting curve was determined planimetrically. The coeff. of variation for 10 different chromatograms bearing 60 μg of each element were, for Zn, 2·1%, for Ga, 3·8%, and for In, 6·9%, and the limiting concn. were 0·33 μg for Zn, 0·30 μg for Ga, and 8·9 μg for In. In the "impulse-rate" method the intensity of fluorescence was determined for each element on the stationary chromatogram. The spots could be rendered visible with 8-hydroxyquinoline without affecting the accuracy. Coeff. of variation for 10 chromatograms (60 μg of each element) were, for Zn, 2·0%, for Ga, 2·4%, and for In, 1·9%. The limiting concn. were 0·34 μg for Zn, 0·10 μg for Ga, and 10·4 μg for In. The impulse-rate method is simpler and quicker, but with large spots the impulse - R_F diagram method is more accurate. The indirect measurement of spots of organic compounds is briefly discussed. A. J. BENNETT

3992. **Improved automatic scanner for the quantitative evaluation of two-dimensional radio-chromatograms.** M. Frank (Ist. Sup. San., Lab. di Elettronica e Chim. Biol., Roma, Italy). *R.C. Ist. Sup. Sanit.*, 1960, **23** (10–11), 893–905.—An improved electronic automatic scanning device is described and full engineering drawings and circuit diagrams are reproduced. The radio-chromatogram is set on the carriage of an electric typewriter so that it is moved across two Geiger counters by the movement (timed) of the typewriter carriage. The number of pulses per time-unit of exploration is recorded in corresponding positions by an electronically-linked actuation of the typewriter number keys. The reproducibility of the results obtained is discussed in detail. E. C. APLING

3993. **Application of chromatography to the analysis of gas mixtures extracted from metals by vacuum fusion under reducing conditions.** C. Baqueé and L. Champeix (Centre d'Études Nucl. de Saclay, France). *Rev. Métall.*, 1960, **57** (10), 919–923.—Nitrogen, CO and H are satisfactorily separated by a column packed with Linde molecular sieve 13X. Reproducibility of the results is good if the column is kept dry. The smallest measurable amounts of N and CO are ≃2 cu. mm, and of H 0·05 cu. mm. Known gas mixtures were analysed by chromatography and by the classical Nash method (*Ind. Eng. Chem., Anal. Ed.*, 1946, **18**, 505);

the precision of each method was $\simeq \pm 1\%$. The values for H obtained by chromatography were rather higher, but the differences remained within the range of error of the methods.

A. J. BENNETT

3994. **Simple apparatus for the gas chromatography of polyphenyls.** R. W. Wilkinson and J. A. Winter. A.E.R.E. Report AERE-M820, 1961. 13 pp.—The apparatus described comprises an alumina-packed, stainless-steel U-tube, model-engine glow-plugs in a Wheatstone bridge circuit, a laboratory furnace and a sample holder; helium is used as carrier gas. The use of the equipment is illustrated by the analysis of polyphenyl waxes; results are given.

G. P. MITCHELL

3995. **Adsorption characteristics of some gas - liquid chromatographic supports.** E. M. Bens (Res. Dept., Chem. Div., U.S. Naval Ordnance Test Sta., China Lake, Calif., U.S.A.). *Anal. Chem.*, 1961, **33** (2), 178–182.—A study was made of different solid supports in an investigation of the causes of tailing in gas - liquid chromatographic separations. C-22 firebrick, glass spheres and Tide detergent were examined and the retention times of some aliphatic and aromatic hydrocarbons, alcohols and ketones on these supports are plotted against inverse temperature, all producing linear isotherms. It is shown that gas - solid elution data are more erratic than those of gas - liquid chromatography, and small amounts of residual samples cause non-reproducible effects on subsequent chromatograms.

C. B. BAINES

3996. **Modification of an ionisation chamber gas - liquid chromatography instrument.** B. T. Cole (Biol. Div., Nat. Lab., Oak Ridge, Tenn., U.S.A.). *Anal. Chem.*, 1961, **33** (2), 317–318.—The use of heating units to maintain column temperatures is described. The voltage to each unit is independently controlled by Variac transformers, the temperature of the upper half of the vapour jacket being kept as close as possible to the boiling-point of the solvent. Two sample-injection systems are described, each providing a tight gas-flow system into which accurately measured samples of 1 μl or less may be injected without introducing air or interrupting the gas flow.

C. B. BAINES

3997. **Recording integrator for gas chromatography.** A. P. H. Jennings (The Distillers Co. Ltd., Res. & Dev. Dept., Epsom, England). *J. Sci. Instrum.*, 1961, **38** (2), 55–58.—Circuit details are given of an instrument based on the velodyne principle in which the speed of a motor is caused to be proportional to the signal to be integrated. The total number of revolutions of the motor shaft during a given period is proportional to the time integral during this period. The integral is recorded continuously in analogue form, on the same chart as the input signal, by means of a duplex recorder. An accuracy of $\pm$ 0·5% is obtained.

G. SKIRROW

3998. **Quantitative evaluation by the flame-ionisation detector.** H. Bredel (V.E.B., Geophys. d. Staatl. Geolog. Komm., Leipzig). *Chem. Tech., Berlin*, 1961, **13** (1), 46–47.—A method is described for the accurate determination of the components of hydrocarbon mixtures from the results of flame-ionisation chromatography. It is based on the fact that a linear relationship exists between the number of C atoms in a hydrocarbon component and the reduced-peak area of that component in the chromatogram, defined as the actual peak area divided by the retention time of the compound. The method does not distinguish between isomeric hydrocarbons, as they have equal reduced-peak areas. The derivation and the use of the necessary equations are described. The method is generally applicable to org. compounds the reduced-peak areas of which vary linearly with the number of C atoms.

H. L. WHITEHEAD

See also Abstracts—**3560**: *Section II*, Evaluation of paper chromatograms by β-ray reflection. **3561**: *Section VI*, Chromatography. **3576**, Inorganic thin-film chromatography.

Optical

3999 **Spectral line width and its use in spectrography.** J. Rubeška and B. Polej (Centr. Geol. Inst., Prague). *Chem. Listy*, 1961, **55** (2), 139–153.—A review, with 45 references.

J. ZÝKA

4000. **Gas identification with micro-wave excitation and a small spectroscope camera.** J. W. Mellichamp, I. Adams and G. A. Wolff (U.S. Army Signal Res. and Development Lab., Fort Monmouth, N.J., U.S.A.). *Appl. Spectroscopy*, 1961, **15** (2), 52–53.—By combining a micro-wave excitation source with a small spectroscope mounted in focus to a 35-mm camera, unknown gases can be identified by their emission spectra. A suitable portable assembly is described and illustrated. The source is a magnetron unit (10 to 100 W, 2450 megacycles per sec.) and the spectroscope covers the visible region with $\simeq$ 15 mm total dispersion and a resolution of $\simeq$ 2 A in the region of 4300 A. The spectrograms of the gases, *e.g.*, from an electronic valve or a sealed discharge tube containing reaction products, are compared with standard spectrograms. Spectral lines and band-heads can be accurately located by means of superposed calibrated scale.

W. J. BAKER

4001. **Stroboscopic studies of the spectra of arc discharges between electrodes of different materials.** L. I. Kiselevskii. *Trudy Khim. i Khim. Tekhnol.*, 1959, (2), 357–361; *Ref. Zhur., Khim.*, 1960, (20), Abstr. No. 80,717.—The change with time of the intensities of the lines of elements entering the discharge from the cathode and the anode is compared, when combinations of pure copper, iron, nickel, chromium and tungsten are used as electrodes. A rectified arc was obtained from generator PS-39 by increasing the resistance in the transformer feed circuit. The stroboscopic effect was attained by vibrating a screen with a narrow cut-out in front of the slit of a medium spectrograph. Each point of the slit was illuminated consecutively by light from the same phase of the discharge, with a resolution of 8° to 10° per phase. The electrodes were sharpened to truncated cones and were set up vertically; the arc current was 3 amp., and the arc gap 1·5 mm. There was no preliminary ignition. The lines were subjected to photometry along the length at intervals corresponding to 10° of phase. The change in the intensities of the lines of the rectified arc is similar to the changes in the normal a.c. arc. In the initial stage of the discharge the predominant lines are due to ions and lines with higher excitation energies. The intensities of homologous lines of the metal anode and the metal cathode change differently during the sparking; in the initial stage the lines of the cathode are more intense and, in the last stage, the anode lines are more intense. This is

explained by a difference in the mechanism by which the material from the positive and negative electrodes enters the discharge plasma. It is suggested that the material leaves the cathode mainly by an electro-erosion process, and leaves the anode by normal evaporation. C. D. KOPKIN

4002. **Comparison of ignited arc sources.** T. P. Schreiber and B. W. Joseph (Res. Lab., General Motors Corp., Warren, Mich., U.S.A.). *Appl. Spectroscopy*, 1961, **15** (1), 8–10.—A conventional ignited unidirectional arc, a Multisource and a Bardócz BIG-210 ignited arc source are compared for the determination of 0·0003 to 0·004% of B in steel and 5% of Sn and 10% of Sb in a lead alloy. The BIG-210 differs mainly in that the igniting spark is derived from a Tesla transformer and contributes little to the sample excitation, and is electronically controlled so that the time of ignition can be varied to produce arc current pulses of varying duration. The conventional arc source is shown to be better for the determination of B, while the BIG-210 gave the best reproducibility for the determination of Sn, with a coeff. of variation of $\simeq 1\%$, and was equal to the Multisource for the determination of Sb, with a coeff. of variation of $\simeq 1{\cdot}7\%$. P. T. BEALE

4003. **Direct-current arc analysis. Some effects of replacing graphite with carbon.** D. C. Spindler (Ferro Corp., Cleveland 5, Ohio, U.S.A.). *Appl. Spectroscopy*, 1961, **15** (1), 20–21.—The effect of using carbon or graphite for the crater electrode, counter-electrode or the added buffer is shown in a total combustion method for titanium oxide. In general, the burn is faster with carbon craters and slower with a carbon buffer. The intensity ratios of W 2944·3 to Ti 2874·2 are higher with carbon craters, and graphite counter-electrodes give brighter spectra. The latter effect was not confirmed with a ground porcelain-enamel sample mixed with graphite and vanadium pentoxide, when carbon and graphite counter-electrodes produced nearly indistinguishable spectra.
P. T. BEALE

4004. **Potassium bromide pellet holder.** R. A. Pittman (U.S. Dept. of Agric., New Orleans, La., U.S.A.). *Appl. Spectroscopy*, 1961, **15** (2), 55.—Dimensioned diagrams are given for the construction of two brass pellet-holders (one for the sample and one for the blank), which can be mounted in the sample chamber of a spectrophotometer so that each will pass the full beam of the instrument.
W. J. BAKER

4005. **Cement-coated wheel technique for spectrographic analyses.** W. R. Neuhaus (Linde Company, Div. of Union Carbide Corp., Tonawanda, N.Y., U.S.A.). *Appl. Spectroscopy*, 1961, **15** (2), 54–55.—To ensure standard sampling and excitation conditions in the spectrographic analysis of alloys, especially those of aluminium, the sample is reduced to uniform filings (100 mesh) and $\simeq 150$ mg of these is glued (with rubber cement) to a graphite-wheel electrode and then sparked. The procedure is described, and the excitation source, exposure conditions and lines for analysis and internal standard are given for the determination of Mg, Mn, Si, Cr and Cu in an aluminium alloy. W. J. BAKER

4006. **Sensitometric properties of a Polaroid emulsion as applied to spectroscopic analysis.** F. R. Bryan and E. F. Runge (Ford Motor Co., Dearborn, Mich., U.S.A.). *Appl. Spectroscopy*, 1961, **15** (1), 16–18.—Spectral sensitivity, contrast, speed and resolution are examined with a "one-minute" daylight processed film that gives a direct positive transparency. The useful range appears to be from 6000 to 3000 A, below which there is a rapid fall in sensitivity. A variation in contrast (γ) from 2·0 to 2·6 is shown in the 3000 to 4000-A region. A coeff. of variation of 4·5% was obtained when the film was used in the determination of 1% of Ni in steel. P. T. BEALE

4007. **Study of interferences in emission and absorption flame photometry.** C. A. Baker and F. W. J. Garton [U.K.A.E.A. (Res. Group), Chem. Div., Woolwich Outstation]. A.E.R.E. Report AERE-R3490, 1961. 21 pp.—A description is given of a double-beam atomic absorption apparatus, and its associated burners, which has been used to study the interference effects, in emission and absorption, of phosphate ions on calcium and strontium determinations. An hypothesis is advanced to account for (*a*) the mechanism of these suppression effects and (*b*) their reduction by various added agents.
G. P. MITCHELL

4008. **Improvements in or relating to spectrometers.** Ontario Research Foundation [Inventor: W. W. B. Schumacher]. Brit. Pat. 865,033; date appl. 24.3.59.—A spectrometer capable of detecting radiation over the range from 0·1 to 150,000 A, including X-rays, infra-red rays, visible light and ultra-violet rays, is described. J. M. JACOBS

4009. **Purification of ethanol and cyclohexane for ultra-violet spectrophotometry.** J. M. Puigmartí-Codina. *Afinidad*, 1960, **17**, 287–295.—*Procedure for ethanol*—To 850 to 900 ml of sample add 25 to 30 drops of Br and set aside overnight. If no Br then remains, add a further 10 to 20 drops and, if the soln. is not decolorised after 1 hr., add $\simeq 0{\cdot}5$ g of zinc powder, with stirring. Then add 8·5 to 9·0 g of NaOH, and some aluminium turnings to facilitate boiling. Heat under reflux for 1 hr. in a flask equipped with distillation column having 7 to 8 theoretical plates, or for 1·5 to 2 hr. with a column having 4 to 6 plates. If a preliminary survey shows the presence of much acetone in the sample, refluxing must be continued for a longer time. Distil, rejecting the first 25 ml of the distillate (at a reflux ratio of 20:1 or 10:1) and collect two further fractions with a slightly lower reflux ratio. Collect a fourth fraction at a reflux ratio of 5:1 or 3:1, and then distil the bulk of the liquid at a reflux ratio of 2:1 (reducing to 1:1) and leaving $\lesssim 50$ ml in the distilling flask. Measure the transmission of the final distillate against water at 210 to 300 mμ or at 220 and 270 mμ. The transmission should not be less than 60% at 220 mμ and not appreciably less than 100% at 260 mμ. If the second, third and fourth fractions are satisfactory they may be added to the main distillate. *Procedure for cyclohexane*—Stir 1 litre of a sample (containing $< 1\%$ of benzene) with 100 ml of 98% H_2SO_4 - 68% HNO_3 (1:1), then shake the mixture with water until the aq. layer is colourless (3 or 4×100 ml). Dry the solvent layer over $CaCl_2$ for some hours, with occasional shaking. Filter and heat under reflux for 1 hr. with a few aluminium turnings. Reject the first 50 ml of distillate, with a reflux ratio of 1:1 or more. Distil two more 50-ml portions, and then distil the bulk of the liquid at a reflux ratio of 1:5 or 1:3, changing to 1:1 and finally, when about 100 ml of solvent remains, to 1:0, leaving a residue of 50 ml. Measure the transmission at 210 to

300 mμ, or at 250 and 220 mμ. The bulk of the distillate should have a transmission $<50\%$ at 220 mμ. L. G. L. UNSTEAD-JOSS

4010. **Spectrophotometric system.** Beckman Instruments, Inc. Brit. Pat. 864,981; date appl. 3.10.58. U.S.A., date appl. 24.2.58.—A double-monochromator spectrophotometer combining a prism and a grating, which is particularly useful in the infra-red region, is described. J. M. JACOBS

4011. **Application of the pressed disc technique for obtaining infra-red spectra of eluates from paper chromatograms.** D. Doskočilová (Res. Inst. of Antibiotics, Roztoky u Prahy, Czechoslovakia). *Chem. Listy*, 1961, **55** (2), 193–200.—The construction of a device for pressing KBr discs is described, as well as the procedure for the homogenisation of the sample with KBr by freeze-drying. The method is suitable for the measurement of the i.r. spectra of $\simeq 1$ mg of, *e.g.*, antibiotics after their isolation by extraction and paper chromatography. J. ZÝKA

4012. **Light source, excitation and high-temperature cell assembly for Raman spectroscopy.** G. J. Janz, Y. Mikawa and D. W. James (Dept. of Chem., Rensselaer Polytech. Inst., Troy, N.Y., U.S.A.). *Appl. Spectroscopy*, 1961, **15** (2), 47–52.—The following are described and illustrated—(*i*) a Toronto-type light source and excitation assembly and circuits for use with a Hilger recording Raman spectrometer, and (*ii*) a simple Raman cell for use up to 575° in the space (10 in. long, 3 in. in diam.) defined by the Toronto arc. The gradient of this cell is $\pm 5°$ at 375° and $\pm 2°$ at 300°; the rate of flow of gas is critical for ensuring optimum efficiency at each temp. The entire assembly should be adaptable to any Raman spectrograph and, with modification, to temp. up to 1600°.
W. J. BAKER

4013. **Improvements in and relating to polarimetry and polarimeters.** J. Bor. Brit. Pat. 866,091; date appl. 29.4.58.—Light from the polariser is passed through a rotator of the plane of polarisation and then through an analyser. In this way a number of different wavelengths may be used.
J. M. JACOBS

4014. **Fluorimetry. V. Quinine sulphate as fluorescence standard. Measurement of the intensity of its fluorescence in aqueous and acetic acid solutions with additions of sulphuric and perchloric acids. Influence of buffer mixtures.** J. Eisenbrand (Chem. Untersuchungsamt f. d. Saarland, Saarbrücken). *Z. anal. Chem.*, 1961, **179** (3), 170–175 (in German).—A constant fluorescence intensity in aq. quinine sulphate soln. can be obtained only at pH >2. The intensity is not affected by phosphate buffers but is slightly quenched by phthalate buffers. The intensity is constant in 0·01N to 0·2N-H_2SO_4 and increases at higher concn. In aq. $HClO_4$ a similar range of constant intensity cannot be obtained, as variation occurs at concn. >0·02N. If glacial acetic acid is used as solvent instead of water, the fluorescence intensity is greater, and is constant over the range 0·01N to 1·0N-$HClO_4$. Such soln. may be useful as fluorescence standards. The lower intensities obtained in aq. soln. may be due to quenching of the fluorescence by water.
A. J. BENNETT

4015. **Highly accurate continuous-recording differential refractometer.** F. A. Vandenheuvel and J. C. Sipos (Fisheries Res. Board of Canada, Technol. Sta., Halifax, Nova Scotia). *Anal. Chem.*, 1961, **33** (2), 286–291.—An instrument capable of 0·5% accuracy in measuring differences in the refractive index of flowing soln. is described. Design details are outlined and performance results are given for the continuous analysis of chromatographic elutions. Mechanical, optical, thermal and electrical noise is considered and controlled by a special device. Reference and unknown-liquid cell compartments are of equal and small vol. (50 μl) and the apparatus is capable of measuring $1 \times 10^{-4}\Delta n$ as a full-scale deflection. Noise level is reduced to $5 \times 10^{-7}\Delta n$.
C. B. BAINES

See also Abstracts—**3561**: *Section VIIa*, Optical methods. **3562**: *Section VIIb*, Emission spectrographic methods. **3991**. Use of X-ray emission spectrography in paper chromatography.

Electrical

4016. **Improvements to the cathode-ray polarograph.** J. E. Seaborn [U.K.A.E.A. (Res. Group), Chem. Div., Woolwich Outstation]. A.E.R.E. Report AERE-R 3630, 1961. 8 pp.—The disadvantages associated with a rapid potential sweep at a dropping-mercury cathode are discussed. Circuits are given that compensate for the effects of cell capacity and preceding ion reduction. These improvements allow greater ease and accuracy of measurement at high sensitivities, there is a greater tolerance to preceding reductions (max. concn. ratio increased from 50:1 to 10,000:1) and solutions may now be examined with reversed potential sweep. G. P. MITCHELL

4017. **Pulse polarography.** G. C. Barker and A. W. Gardner (Chem. Div., A.E.R.E., Harwell, England). A.E.R.E., Report C/R 2297, 1961. 24 pp.—The a.c. procedure described gives an improved normal polarogram and also a derivative polarogram. For normal polarograms, the cell voltage is kept generally constant, but about 2 sec. after the fall of each mercury drop it is changed by a polarising pulse (0·04 sec.) to a value that becomes increasingly negative with time. The change in diffusion current produced by each pulse during the second half of the pulse-life is measured electronically. Reversibly and irreversibly reduced ions can thus be detected at concn. as low as 10^{-7}M, and a minor ion can be detected or determined in the presence of a much higher concn. of an ion that is reduced at a more positive potential. For derivative polarograms, small pulses of constant amplitude (>50 mV) are superposed on a slowly changing voltage, thus permitting reversibly reduced ions to be detected at concn. as low as 10^{-8}M.
W. J. BAKER

4018. **Simple micro-volumetric combustion polarographic cell.** R. M. Parkhurst (Stanford Res. Inst., Menlo Park, Calif., U.S.A.). *Anal. Chem.*, 1961, **33** (2), 320.—Weighing, combustion, dilution and polarography of materials such as biological samples, foods, plant tissues, organic salts and metal organic chelates can be carried out in the micro-cell described.
C. B. BAINES

4019. **Improvements in apparatus for use in measuring pH values.** G. Kent, Ltd. [Inventors: C. Chalmers, D. A. Rudd and R. S. Medlock]. Brit. Pat. 863,605; date appl. 6.6.56.—One of the two parts of the electrode holder described in Brit. Pat. 695,991 is provided with a metal tube, which defines a wall of the chamber, and with a metal sealing ring which is compressed against that tube by a

surface on the other part of the holder. The seals between the electrodes and the other part of the holder are provided by metal sleeves disposed about the electrodes and sealed to them and to that part of the holder. J. M. JACOBS

4020. **Automatic continuous measurement and control of pH by means of steam-sterilisable glass electrodes.** G. Gualandi, E. Caldarola and E. B. Chain (Ist. Sup. San., Centro Int. di Chim. Microbiol., Roma, Italy). *R.C. Ist. Sup. Sanit.*, 1960, **23** (10–11), 869–892.—The construction and use of a specially robust and readily sterilisable glass electrode - reference electrode system is described. The glass electrode is a modification of a commercial heat-resistant glass electrode, equipped with an internal silver - silver chloride - satd. KCl half-cell, and fitted into a stainless-steel sleeve, sealed with washers of Teflon and silicone rubber. The reference electrode employs the same half-cell, but has a piece of asbestos fibre, or a fine cylinder of porous porcelain, sealed into the glass at the base of the electrode, to form an electrical junction. The electrodes show no significant alteration in sensitivity after repeated steam-sterilisation. E. C. APLING

4021. **Theory of stripping voltammetry with spherical electrodes.** W. H. Reinmuth (Dept. of Chem., Columbia Univ., New York, U.S.A.). *Anal. Chem.*, 1961, **33** (2), 185–187.—The theory of this technique is discussed and two sources of deviation from planar electrode behaviour are shown, namely, curvature of the electrode and its volume. The range of application and spherical correction formulae are given for chronopotentiometry and hanging-drop polarography. C. B. BAINES

4022. **Stripping analysis with spherical mercury electrodes.** I. Shain and J. Lewinson (Chem. Dept., Univ. of Wisconsin, Madison, U.S.A.). *Anal. Chem.*, 1961, **33** (2), 187–189.—The concn. of amalgamated metal within a hanging-mercury-drop electrode, resulting from the pre-electrolysis stage in stripping analysis, is shown to be higher than in planar electrodes. This concn. is uniform and an equation is given for its calculation. This, combined with the theory of the stripping process, is useful in developing new methods of stripping analysis. The theoretical and experimental curves are compared for the determination of Tl^+. C. B. BAINES

4023. **Titration of acids and bases with metal - metal oxide electrodes.** O. M. Podurovskaya and V. E. Petrakovich (State Sci. Res. and Development Inst. of the Nitrate Ind. and Products of Org. Synthesis). *Zavod. Lab.*, 1961, **27** (2), 157–159.—Work with platinum and molybdenum electrodes which are oxidised before a titration by being heated in the flame of a spirit burner is described. With a mixture of an org. acid and a mineral acid, potentiometric titration in 70% acetone soln. yields two distinct branches of the titration curve. Contents can be determined with an accuracy of 0·5% of the theoretical. G. S. SMITH

4024. **Glass indicator-electrode for the direct titration of potassium with calcium tetraphenylborate.** R. Geyer and H. Frank (Inst. f. Anal. Chemie, Tech. Hochsch. für Chemie, Leuna-Merseburg). *Z. anal. Chem.*, 1961, **179** (2), 99–105 (in German).—An electrode constructed from glass containing 62% of SiO_2, 33% of Na_2O and 5% of Al_2O_3 is reported to be sensitive to K^+. It is insensitive to pH changes over the range 7 to 9·5, and at pH $\simeq$ 7 is almost insensitive to Ca^{2+} although it responds to large amounts of Na^+ and also to K^+. Potassium (20 to 40 mg) may be determined in the presence of large amounts ($\simeq$1 g) of Ca^{2+} or Mg^{2+} by potentiometric titration with 0·1N-Ca tetraphenylborate. Sodium interferes with the determination of very low concn. of K^+. T. R. ANDREW

4025. **Method for determination of equivalence-point in potentiometric titrations.** J. M. H. Fortuin (Staatsmijnen in Limburg, Geleen, Netherlands). *Anal. Chim. Acta*, 1961, **24** (2), 175–191 (in English).—Equations are developed for calculating the end-point of potentiometric titrations. The influence of dilution is studied. The method requires no graphical representation and leads to approx. values for ionisation constants. H. N. S.

4026. **Resolution of time-dependent γ-spectra with a digital computer and its use in activation analysis.** O. U. Anders and W. H. Beamer (Radiochem. Lab., Dow Chemical Co., Midland, Mich., U.S.A.). *Anal. Chem.*, 1961, **33** (2), 226–230.—A small electronic digital computer is described for the correction, normalisation and resolution of time-dependent γ-spectra from short-irradiation-time neutron-activation samples. By its use, maximum information from mixed γ-spectra and freedom from simultaneous irradiation of elemental standards are obtained. The analysis of two samples, taking 2 hr., is described. Reference spectra are available for 69 elements. C. B. BAINES

4027. **Liquid-sampling device for the mass spectrometer.** N. R. Mumbach (Res. Lab., Linde Co., Div. of Union Carbide Corp., Tonawanda, N.Y., U.S.A.). *Anal. Chem.*, 1961, **33** (2), 318–319.—An apparatus is described for the sampling of liquids of relatively high boiling-points which ensures that the vapour entering the spectrometer has the same composition as the original sample and is not contaminated with stop-cock grease. The device has been satisfactory in the analysis of mixtures of alcohols. C. B. BAINES

4028. **Mass spectrometer for the isotopic analysis of lithium.** R. G. Ridley and D. E. P. Silver (Atomic Weapons Res. Est., Aldermaston, England). *J. Sci. Instrum.*, 1961, **38** (2), 47–51.—Details are given of a 60° magnetic mass spectrometer designed to measure the abundances of the lithium isotopes of masses 6 and 7. Lithium nitrate is ionised in a thermal ionisation source and the two ion beams are individually collected on two separate collectors. The beams are pulsed and the output pulses amplified and subtracted from one another, and the difference signal is displayed on a cathode-ray tube. Attenuators are adjusted until the difference signal is zero and the isotopic ratio is then given by the ratio of the attenuator settings for the two beams. Corrections are made for unequal transmission through the spectrometer and for inequalities in the circuitry. The isotope ratio can be measured with a precision of $\pm$0·7%. G. SKIRROW

See also Abstracts—**3560**: *Section II*, Analytical use of isotopes. **3561**: *Section Vb*, Adsorption at dropping mercury electrode. Action of tetra-ethylammonium salts in polarography. *Section VIIa*, Mass-spectrometric gas analysis.

ABBREVIATIONS

Certain abbreviations in everyday use are not included in the following list. When any doubt might arise from the use of an abbreviation or symbol the word is printed in full.

alternating current	a.c.
ampere	amp.
Ångström unit	A
anhydrous	anhyd.
approximate, -ly	approx.
aqueous	aq.
atmospher-e, -ic	atm.
boiling-point	b.p.
British thermal unit	B.Th.U.
calorie (large)	kg-cal.
calorie (small)	g-cal.
centimetre	cm
coefficient	coeff.
Colour Index	C.I.
concentrated	conc.
concentration	concn.
constant	const.
crystalline / crystallised	cryst.
cubic	cu.
current density	c.d.
cycles per second	c/s
density	ρ
density, relative	d or wt. per ml
dilute	dil.
direct current	d.c.
distilled	dist.
electromotive force	e.m.f.
equivalent	equiv.
ethylenediaminetetra-acetic acid	EDTA
gram	g
gram-molecule	mole
half-wave potential	$E_{\frac{1}{2}}$
hour	hr.
hydrygen ion exponent	pH
infra-red	i.r.
insoluble	insol.
international unit	i.u.
kilogram	kg
kilovolt	kV
kilowatt	kW
liquid	liq.
maxim-um, -a	max.
melting-point	m.p.
microgram	μg (not γ)
microlitre	μl
micromole	μmole
micron	μ
milliampere	mA
milli-equivalent	milli-equiv.
milligram	mg
millilitre	ml
millimetre	mm
millimicrogram	mμg
millimolar	mM
millivolt	mV
minute (time)	min.
molar (concentration)	M
molecul-e, -ar	mol.
normal (concentration)	N
optical rotation	α_l
ounce	oz
parts per million	p.p.m.
per cent.	%
per cent. (vol. in vol.)	% (v/v)
per cent. (wt. in vol.)	% (w/v)
per cent. (wt. in wt.)	% (w/w)
potential difference	p.d.
precipitate (as a noun)	ppt.
precipitated	pptd.
precipitating	pptg.
precipitation	pptn.
preparation	prep.
qualitative, -ly	qual.
quantitative, -ly	quant.
recrystallised	recryst.
refractive index	n_λ^t
relative band speed	R_B
relative humidity	r.h.
revolutions per minute	r.p.m.
saponification value	sap. val.
saturated calomel electrode	S.C.E.
second (time)	sec.
soluble	sol.
solution	soln.
specific gravity	sp. gr.
specific rotation	$[\alpha]_\lambda^t$
square centimetre	sq. cm
standard temp. and pressure	s.t.p.
temperature	temp.
ultra-violet	u.v.
vapour density	v.d.
vapour pressure	v.p.
volt	V
volume	vol.
watt	W
wavelength	λ
weight	wt.

In addition, the following symbols may be used in conjunction with numerical values or in mathematical expressions—

greater than	$>$	less than	$<$
not greater than	$\ngtr$	not less than	$\nless$
is proportional to	$\propto$	of the order of, approximately	$\simeq$

The principal Pharmacopoeias are denoted by B.P., U.S.P. or D.A.B., together with the identifying roman numeral or year.

Valency states are represented by a superscript roman numeral, *e.g.*, Fe^{II}, Mo^{III}. Substances in the ionic state are represented by Na^+, Fe^{2+}, Fe^{3+}, etc., for cations and by Cl^-, SO_4^{2-}, PO_4^{3-}, etc., for anions.

The chemical nomenclature used in the abstracts is that recommended by The Chemical Society ("Handbook for Chemical Society Authors", The Chemical Society, London, 1960), and may differ from that used in the original articles.

Volume 8. No. 9, Abstracts 3560 – 4028 September, 1961

ANALYTICAL ABSTRACTS

A PUBLICATION OF
THE SOCIETY FOR ANALYTICAL CHEMISTRY

EDITORIAL COMMITTEE

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Members: B. S. Cooper, C. H. R. Gentry, C. A. Johnson, H. F. W. Kirkpatrick, B. J. Walby, W. A. Waygood, K. A. Williams
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No. 98 September, 1961

THE SOCIETY FOR ANALYTICAL CHEMISTRY

BULLETIN

FORTHCOMING MEETINGS

Ordinary Meeting of the Society, October 5th and 6th, 1961

An Ordinary Meeting of the Society will be held on Thursday and Friday, October 5th and 6th, 1961, at The Institution of Mechanical Engineers, Birdcage Walk, London, S.W.1.

The subject of the meeting will be **"Advances in Analytical Chemistry**: Selected Topics Originating from Analytical Requirements in the Field of Nuclear Technology."

Programme

October 5th

2.30 *p.m. to* 4.30 *p.m.*: *First Session*—

"Studies of the Boron - Curcumin Complex and its Use in Trace Boron Analysis," by M. R. Hayes, A.R.I.C., and J. Metcalfe, B.Sc.

"Applications of Micro-coulometry," by R. G. Monk, A.R.C.S., D.I.C., Ph.D., K. C. Steed and G. C. Goode, B.Sc., A.R.I.C.

"The Gravimetric Determination of Uranium as the Phosphate," by J. S. Wright, J. A. Ryan, A.R.I.C., and T. J. Hayes, A.R.I.C.

5.15 *p.m. to* 7.15 *p.m.*: *Second Session*—

"A Study of the Determination of Oxygen in Beryllium by Vacuum Fusion," by M. R. Everett and J. E. Thompson.

"The Application of the Conductimetric Method for the Determination of Carbon to Highly Alloyed Steels and the Less Common Metals," by J. E. Still, B.Sc., F.R.I.C., and I. R. Green, A.R.I.C.

"The Identification and Determination of Foreign Phases and Constituents in Metals, with Special Reference to Beryllium," by H. P. Rooksby, B.Sc., F.Inst.P., and I. R. Green, A.R.I.C.

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"Suspension Scintillation Counting of Carbon-14 Barium Carbonate," by H. J. Cluley, Ph.D., F.R.I.C.

"The Use of Isotope Dilution for the Determination of Hydrogen in Metals with Particular Reference to Alkali Metals," by C. Evans, B.Sc., Dip.Chem.Eng., and J. Herrington, B.Sc.

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"The Use of Isotope Dilution for the Determination of Hydrogen in Metals with Particular Reference to Alkali Metals," by C. Evans, B.Sc., Dip.Chem.Eng., and J. Herrington, B.Sc.

2.30 *p.m. to* 4.30 *p.m.*: *Fourth Session*—

"Reverse Phase Partition Chromatography," by T. J. Hayes, A.R.I.C., and A. Hamlin, B.Sc., F.R.I.C.

"Gas Chromatography in the Analysis of Inorganic Systems," by T. R. Phillips, Ph.D., B.Sc., and G. Iveson.

"The Analysis of Nuclear Reactor Carbon Dioxide for Gaseous Impurities," by R. M. S. Hall, M.A., A.R.I.C., A.Inst.P.

Joint Meeting of the Society with the Infra-red Discussion Group, December 15th, 1961

A JOINT Meeting of the Society with the Infra-red Discussion Group will be held at 11.15 a.m. on Friday, December 15th, 1961, at King's College, Strand, London, W.C.2.

The subject of the meeting will be **"Applications of Infra-red Spectroscopy to Quantitative Analysis"** and the following papers will be presented and discussed in two sessions—

Introductory Paper on "The Principles of Quantitative Infra-red Spectroscopy," by Dr. W. R. Ward.

"Quantitative Infra-red Analysis of Agricultural Chemicals," by P. G. Marshall.

"Quantitative Analysis of Milk and Other Emulsions by Infra-red Absorption," by Dr. J. D. S. Goulden.

"Quantitative Infra-red Analysis of Phosphonitrilic Chloride Polymers," by Dr. A. C. Chapman.

"Some Uses of Infra-red Spectroscopy in the Pharmaceutical Industry," by Dr. H. D. C. Rapson.

We shall be grateful if those who are hoping to attend this meeting will notify the Assistant Secretary, The Society for Analytical Chemistry, 14, Belgrave Square, London, S.W.1, not later than **Monday, October 9th, 1961.**

Ordinary Meeting of the North of England Section, September 30th, 1961

AN Ordinary Meeting of the Section will be held at 2.15 p.m. on Saturday, September 30th, 1961, at the City Laboratories, Mount Pleasant, **Liverpool, 3**.

The following paper will be presented and discussed—

"Some Analytical Problems in the Baking Industry," by R. A. Knight, B.Sc., F.R.I.C.

Joint Meeting of the North of England Section and the Physical Methods Group, October 10th, 1961

A JOINT Meeting of the North of England Section and the Physical Methods Group will be held at 7 p.m. on Tuesday, October 10th, 1961, in the Conference Room of the British Iron and Steel Research Association, Hoyle Street, **Sheffield, 3**.

The following papers will be presented and discussed—

"Application of Atomic Absorption Spectrophotometry to Metallurgical Analysis," by W. T. Elwell, F.R.I.C.

"Some Interferences in Flame Photometry," by M. S. W. Webb, B.Pharm., F.P.S., F.R.I.C., and P. C. Wildy, B.Sc.

The meeting will be preceded at 2.30 p.m. by a visit to the United Steel Companies Research Laboratories, Swinden House.

Joint Meeting of the North of England Section and the North Lancashire Section of the Royal Institute of Chemistry, October 27th, 1961

A JOINT Meeting of the North of England Section and the North Lancashire Section of the Royal Institute of Chemistry will be held at 7.30 p.m. on Thursday, October 27th, 1961, in the College for Further Education, **Lancaster.**

The following paper will be presented and discussed—

"The Analysis of Edible Oils Contaminated with Synthetic Ester Lubricants," by G. B. Crump, B.Sc., A.R.I.C.

Joint Meeting of the Scottish Section with the Glasgow Section of the Society of Chemical Industry, October 6th, 1961

A JOINT Meeting of the Scottish Section and the Glasgow Section of the Society of Chemical Industry will be held at 7.15 p.m. on Friday, October 6th, 1961, at the Royal College of Science and Technology, George Street, **Glasgow.**

The subject of the meeting will be **"Pentaerythritol"** and the following papers will be presented and discussed—

"Applications of Pentaerythritol," by A. W. E. Staddon, B.Sc.

"Analysis of Pentaerythritol," by A. F. Williams, B.Sc., F.R.I.C.

Ordinary Meeting of the Scottish Section, October 20th, 1961

AN Ordinary Meeting of the Section will be held at 4 p.m. on Friday, October 20th, 1961, at The University, **Aberdeen.**

The following papers will be presented and discussed—

"Stannous Acetate as a Standard Reductant," by W. Moser, B.Sc., and W. B. Simpson, B.Sc.

"Some Seldom-remembered Aspects of Analytical Techniques," by R. A. Chalmers, B.Sc., Ph.D.

"The Analytical Chemistry of Technetium and Rhenium," by R. J. Magee, M.Sc., Ph.D., A.R.I.C.

Joint Meeting of the Western Section, the Microchemistry Group and the Mid-Southern Counties Section of the Royal Institute of Chemistry, October 20th, 1961

A JOINT Meeting of the Western Section, the Microchemistry Group and the Mid-Southern Counties Section of the Royal Institute of Chemistry will be held at 7.45 p.m. on Friday, October 20th, 1961, at the Red Lion Hotel, **Salisbury.**

The subject of the meeting will be **"Trace Analysis in Archaeology."**

The meeting will be preceded in the afternoon by a visit to Avebury Museum and Site.

Joint Meeting of the Midlands Section and the Birmingham and Midlands Section of the Royal Institute of Chemistry, October 10th, 1961

A JOINT Meeting of the Midlands Section and the Birmingham and Midlands Section of the Royal Institute of Chemistry will be held at 7 p.m. on Tuesday, October 10th, 1961, at The University, Edgbaston, **Birmingham, 15.**

A lecture on "Research Work in Analytical Chemistry at the Technical University of Budapest" will be given by Professor L. Erdey.

Ordinary Meeting of the Midlands Section, October 26th, 1961

AN Ordinary Meeting of the Section will be held at 7 p.m. on Thursday, October 26th, 1961, in the Technical College, **Nottingham.**

The following paper will be presented and discussed—

"Aquametry," by Dr. J. H. Thompson.

Ordinary Meeting of the Physical Methods Group, October 24th, 1961

AN Ordinary Meeting of the Group will be held at 6 p.m. on Tuesday, October 24th, 1961, at Boots Pure Drug Co., Ltd., **Nottingham.**

The subject of the meeting will be **"Determination of Particle Size."**

Ordinary Meeting of the Biological Methods Group, October 18th, 1961

AN Ordinary Meeting of the Group will be held at 7 p.m. on Wednesday, October 18th, 1961, in the Meeting Room of the Chemical Society, Burlington House, Piccadilly, London, W.1.

A lecture on "The Use of Bacteriophages in Epidemiology" will be given by Miss E. Maureen Wilson, B.Sc.

BRITISH STANDARDS INSTITUTION

DRAFT SPECIFICATIONS

A FEW copies of the following draft specifications, issued for comment only, are available to members of the Society, and can be obtained from the Secretary, The Society for Analytical Chemistry, 14, Belgrave Square, London, S.W.1.

Draft Specifications prepared by Panel TLE/5/3/1—Methods of Analysis of Cathode Nickels.

AB(TLE)4922—Draft B.S. Methods for the Analysis of Nickels for use in Electronic Tubes and Valves. Part 6: Determination of Copper.

AB(TLE)4923—Draft B.S. Methods for the Analysis of Nickels for use in Electronic Tubes and Valves. Part 5: Determination of Cobalt (Photometric Method).

AB(TLE)4924—Draft B.S. Methods for the Analysis of Nickels for use in Electronic Tubes and Valves. Part 8: Determination of Manganese.

Draft Specifications prepared by Sub-Committee LBC/11/1—Apparatus for Micro-chemical Combustion Methods.

AB(LBC)5157—Draft B.S. Specification for Simplified Micro-Kjeldahl Apparatus. (B.S. 1428, Part B3)

AB(LBC)5158—Draft B.S. Specification for Nitrogen Determination Apparatus (Micro-Kjeldahl) (Revision of B.S. 1428, Part B1).

COMMUNICATIONS ACCEPTED FOR PUBLICATION IN *THE ANALYST*

THE following communications have been accepted for publication in *The Analyst*, and are expected to appear in the near future.

"The Identification of Small Amounts of Bases in Urine by Infra-red Spectrophotometry," by P. J. Morgan.

"A Simple By-pass Injector for Gas Chromatography," by P. J. Kipping and P. G. Jeffery.

"The Determination of Gold in Mill Products by Means of a Cathode-ray Polarograph," by K. J. Cathro.

"Studies in Precipitation from Homogeneous Solution by Cation Release at Constant pH. Part 1: Oxidation of EDTA Solution by Hydrogen Peroxide," by P. F. S. Cartwright.

"Studies in Precipitation from Homogeneous Solution by Cation Release at Constant pH. Part 2: The Precipitation of Various Metal Phosphates," by P. F. S. Cartwright.

"Further Studies on the Zone - Strip Technique," by I. R. Shimi, G. M. Imam, and A. Dewedar.

"A Vanillin-Perchloric Acid Reagent for Detecting Pregnanetriol and Related Compounds on Paper Chromatograms," by J. D. Few.

"Colorimetric Determination of 'Kelthane' Residues," by J. T. Hughes.

"Colorimetric Determination of Tin in Propellants by Means of Haematoxylin," by G. Norwitz.

"A Method of Eliminating Phosphorus Interferences in the Flame-spectrophotometric Determination of Calcium," by H. B. Heeney, G. M. Ward and A. F. Wilson.

"The Estimation of Cellulose and Household Coal in Town-refuse Compost," by L. J. Mebius.

"Elimination of Interfering Citrate and Mineral Acids in the Spectrophotometric Determination of Phosphorus in Fertilisers," by Sven-Eric Dahlgren.

"Determination of Alkali Polysulphides," by L. Legradi.

"The Determination of Thiamine (Vitamin B_1) in Cereal Products: Further Refinements," by H. N. Ridyard.

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